Oxidizer Classification Research Project:

Tests and Criteria

Final Report

November 2, 2009

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FOREWORD

The purpose of this research project, which was initiated at the request of the NFPA Technical Committee on Hazardous Chemicals, is to develop a scientific and reliable method to classify chemical oxidizers based on the degree to which an oxidizer increases the burning rate of combustible materials with which it comes into contact. A test plan was developed to determine the relationship between oxidizer chemical structure, composition, and packaging on the burning rate of oxidizers for classification and fire protection in storage environments. The resulting classification scheme for oxidizers is practical and includes a bench scale screening test method and medium scale burn testing of the oxidizer in its packaging with criteria for classification.

The Research Foundation expresses gratitude to the report author Elizabeth C. Buc of Fire and Materials Research Laboratory, LLC and to the Project Technical Panelists and sponsors listed on the following page.

The content, opinions and conclusions contained in this report are solely those of the author.

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PROJECT CONTRACTORS AND COLLABORATORS

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FM Global, Norwood, MA
Southwest Research Institute, San Antonio, TX

ACKNOWLEDGMENTS

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EXECUTIVE SUMMARY

Chemical oxidizers are defined as 'any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials and, under some circumstances, can undergo vigorous self-sustained decomposition due to contamination or heat exposure'.[1] Unless properly stored and handled, oxidizers are serious fire safety hazards. In an effort to prevent and/or mitigate fires caused by or involving oxidizers, the NFPA developed a four-class classification system for solid and liquid oxidizers. The first and most important step in applying the Code's requirements for the safe storage of oxidizers is Class assignment. The Class of oxidizer not only provides an indication of the potential fire hazard but also specifies the quantities of material requiring protection under various storage configurations and occupancies. Oxidizers assigned to Class 1 are least hazardous, while those assigned to Class 4 exhibit the most severe physical hazards (i.e., explosive reaction). While in use since 1973, this classification system is subjective. Burning rate, the principal physical hazard of oxidizers used to distinguish between the four Classes, is not defined by the Code and there are no tests for assessing the degree to which an oxidizer increases the burning rate of combustible materials with which it comes into contact.

In 2005, the Hazardous Chemicals Technical Committee (HCS-AAA) initiated a project to develop a new or enhanced system for classifying oxidizers with criteria determined by the use of systematic, measurable test data. The project was undertaken in two phases. Phase I consisted of a comprehensive review of the Code and annex, fires involving oxidizers during transportation and storage, published literature, and test methods for evaluating oxidizer physical hazards.[2] A report of the findings from this review was published in April 2006. The development of reaction-to-fire tests with criteria based on burning rate only to classify oxidizers consistent with the current definitions of Class 1, Class 2, Class 3 and Class 4 was set as the objective of Phase II. The Phase II research proposal and test plan reflected the Committee's desire for development of a reliable and meaningful bench-scale screening test and/or an intermediate-scale fire exposure test. Other specific interests of the Committee included an evaluation of oxidizers common in high-volume commerce and storage and the influence of product form and different combustible test packaging on burning rate.

During Phase II, a bench-scale screening test was developed based on the globally accepted UN Test O.1 method for Division 5.1 solid oxidizers.[3] The bench-scale test was used to perform over 225 screening tests with twenty oxidizers that exhibited a range in burning behavior. Four test-operator-independent variables were used to evaluate burning rate: mass loss rate, burning duration, peak temperature, and flame height. Fifty-nine oxidizer-fuel mixtures were tested using the Fire Propagation Apparatus (FPA, ASTM E 2058[4]) at FM Global. Results from the bench-scale screening test were validated by establishing correlations between mass loss rate and heat release rate data from the FPA. Thirty-two intermediate-scale fire exposure tests based on ASTM E 2067[5] were conducted at Southwest Research Institute (SwRI) with empty packaging, packaged sodium chloride, packaged phenolic resin powder, and fourteen oxidizers in three combustible test packaging types. Most intermediate-scale tests consisted of the same mass (24-lbs) of oxidizer in the same combustible packaging consisting of six high-density polyethylene (HDPE) containers enclosed in doubled-wall corrugated board cartons. Energy released during the fires involving oxidizers at the intermediate-scale was characterized by peak convective heat release rate and the duration of active burning from radiant heat flux profiles.

The proposed oxidizer classification method consists of two reaction-to-fire tests: (1) a bench-scale screening test with 30-g mixtures of oxidizer and dried cellulose powder exposed to a glowing wire and (2) an intermediate-scale test with 24-lbs of oxidizer in combustible test

packaging exposed to a constant external fire source. The data from eleven solid oxidizers, tested at both the intermediate-scale and bench-scale, were evaluated and used to establish criteria for classifying oxidizers. Peak convective heat release rate at the intermediate-scale and maximum mass loss rate at the bench-scale were determined to be the principle indicators of burning rate. The duration of increased burning rate or active burning times were consistent, secondary criteria for classification that distinguished Class 1 oxidizers from Class 3 oxidizers.

The proposed bench-scale screening test can be performed by most laboratories at low cost[*]. The intermediate-scale fire exposure test requires a burn facility. The screening test should be used as a first step to classify oxidizers, followed by confirmatory intermediate-scale tests, especially for oxidizers that are not clearly Class 1 or Class 3. And for safety, the bench-scale screening test should be conducted before intermediate-scale testing.

The mass loss rate and active burning time data from the bench-scale screening test are test-operator-independent indicators of burning rate and are capable of preliminary categorizing an oxidizer according to the fire characteristic in question (i.e., burning rate). The method of collecting mass loss data during combustion has already been subject to inter-laboratory testing. Criteria based on mass loss data were found to be more reliable than the burning time determined with a stop watch. The bench-scale screening test can distinguish between weak or clearly Class 1 oxidizers, strong or clearly Class 3 oxidizers, and oxidizers that principally decompose. It can also be used to investigate the influence of particle size, additives and the degree of hydration or moisture content on burning rate. The intermediate-scale test and the peak convective heat release rate are the best method and measure of the burning rate of the packaged oxidizer, respectively. The larger scale test results were used to establish meaningful criteria for the bench-scale screening test. The intermediate-scale fire exposure test would be required for oxidizers that principally decompose, and are not clearly Class 1 or Class 3. The results of an intermediate-scale fire exposure test with 24 pounds of material in combustible test packaging will determine if an oxidizer is Class 1, Class 2, or Class 3.

Cumulative results indicated that the burning rate of the tested solid oxidizers was principally a function of the oxidizer and its concentration. Inclusive in the influence of the oxidizer and its concentration were the amount and type of additives as well as the degree of moisture content of the oxidizer or hydrated salt additives. The tests and criteria are sensitive enough that formulated or oxidizers mixed with inert materials were distinguishable from the unformulated or pure oxidizer. Product form (granular vs. tablet) did not exhibit as strong an influence on burning rate.

Additional research is required to evaluate fire scenarios involving liquid oxidizers. Because there are fewer liquid phase oxidizers than solid phase oxidizers, it is recommended that the storage, use and handling of these materials be subject to individual fire hazard assessment until which time a test method(s) and criteria based on fire scenario are developed and validated by intermediate-scale tests. Also, Code provisions should be considered for liquid oxidizers that have been identified as explosive precursors.

Results from this project will significantly improve the Code and safety where oxidizers are stored by properly identifying the Class to which an oxidizer or oxidizer-containing product belongs. This research represents the first time bench-scale tests to evaluate chemical oxidizers

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[*] The laboratory should have oxidizer-handling experience, the minimum required equipment requirements and chemical safety training.

were based on intermediate-scale test results and the first time bench-scale tests involving oxidizers mixed with fuels in different concentrations have been studied and validated with fundamental reaction-to-fire properties.

The following table and flow diagram summarize the proposed oxidizer classification tests and criteria resulting from this research project. The bench-scale screening test can be used to classify oxidizers. If the material's maximum mass loss rate and active burning time are not clearly Class 1 or clearly Class 3, then it is a candidate Class 2 oxidizer. A manufacturer can accept Class 2 assignment or proceed to intermediate-scale testing in combustible test packaging to resolve whether the oxidizer is a Class 1, Class 2, or Class 3.

Tests and Criteria for Assigning Solid Oxidizers to Class 1, Class 2, Class 3 and Class 4.

		PROPOSED TESTS AND CRITERIA			
		Bench-Scale Screening Test (30-g mixtures)		Intermediate-Scale Fire Exposure Test (24-lbs in test packaging)	
CLASS	**CURRENT CRITERIA**	Maximum Mass Loss Rate (MLR)* [g/s]	Active Burning Time (t_{active})** [s]	Peak Convective Heat Release Rate (HRR_{conv}) [kW]	Active Burning Time*** [s]
CLASS 1	Does not moderately increase the burning rate of combustible materials	≤0.3	≥30	≤100	≥120
CLASS 2	Causes a moderate increase in the burning rate of combustible materials	0.3<MLR<3	6< t_{active} <30	100-200	60< t_{active} <120
CLASS 3	Causes a severe increase in the burning rate of combustible materials	≥3	≤6	≥200	≤60
CLASS 4	Generally meets the Class 3 criteria plus evidence to support explosive reaction due to contamination or exposure to thermal or physical shock including UN and/or GHS designations.				

* Maximum mass loss rate from 20 to 80% the final measured mass (m_f) of 1:1, 4:1 and 9:1 mixtures.

** Calculated from the mass loss profiles.

***Calculated from the width of the curve at ½ the peak radiant heat flux.

Bench-Scale Screening Tests with Oxidizer:Cellulose Powder Mixtures*

Max $MLR_{20-80\%mf} \leq 0.3g/s$ & active burning time ($t_{0-80\%mf}$) $\geq 30s$

Class 1 or Class 3 criteria not met

Max $MLR_{20-80\%mf} \geq 3g/s$ & active burning time ($t_{0-80\%mf}$) $\leq 6s$

Class 1

Borderline Class 1/Class 2

Class 2

Borderline Class 2/Class 3

Class 3

Intermediate-Scale Fire Exposure Test with 24 lb (10.9 kg) Oxidizer in Test Packaging

Peak Convective HRR ≤ 100 kW & Active burning time $\geq 120s$

Peak Convective HRR ≥ 200 kW & Active burning time $\leq 60s$

Class 1

Class 2

Class 3**

100 kW< Peak Convective HRR< 200 kW
&
60s< Active burning time< 120s

* Thirty-gram (30-g) piles of 1:1, 4:1 and 9:1 by weight mixtures of the oxidizer, with the as-received particle size, and dried cellulose powder. If the 1:1 or 4:1 oxidizer: cellulose powder mixture result in burning durations less than 6 seconds or mass loss rates greater than 3 g/s, testing a 9:1 mixture is not required.

** A Class 4 oxidizer generally meets the Class 3 burning rate criteria plus evidence to support explosive reaction due to contamination or exposure to thermal or physical shock.

Solid oxidizer classification tests and criteria flow diagram.

Recommendations

Assigning an oxidizer to Class 1, Class 2, Class 3 or Class 4 no longer needs to be subjective as the present research proposes a systematic, quantitative method with two reaction-to-fire tests and criteria for evaluating the enhancement or acceleration of burning rate by oxidizers. Based on the results from Phase II of this project, the following recommendations are proposed to the Hazardous Chemicals Technical Committee:

(1)   Adopt the proposed method with two reaction-to-fire tests and criteria for assigning solid oxidizers to Class 1, Class 2, Class 3, or Class 4.

(2)   Evaluate and refine the definitions of oxidizer, burning rate and the definitions of Class 1, Class 2, Class 3, and Class 4 oxidizers based on this report and the proposed tests and criteria.

(3)   Add a summary of this research in the Code's Annex.

(4)   Evaluate the test data and Class of oxidizers that, based on the intermediate-scale test results, differed from their current NFPA Class. These oxidizers are sodium persulfate, calcium peroxide, potassium permanganate, potassium perchlorate and calcium hypochlorite (50 wt%). Under the proposed tests and criteria, each would be one class higher. Further, potassium monopersulfate should be considered for addition to Class 1 in the Code's annex.

(5)   Evaluate the burning rate of ammonium nitrate.

(6)   Establish a technical basis for the existing fire protection provisions with additional testing using Class 1-borderline Class 2 and Class 2-borderline Class 3 oxidizers.

(7)   Modify the Code to provide the same security measures recommended by the NRCan Explosive Act for specific solid and liquid oxidizers identified as explosive precursors. The oxidizers include hydrogen peroxide (≥30%), potassium chlorate, potassium perchlorate, sodium chlorate, nitric acid (≥68%), potassium nitrate, and sodium nitrate.

Disclaimers

Oxidizers have multiple physical and health hazards. The tests and data described in this report provide information only on the 'burning rate' of oxidizers. This report does not address other physical hazards of oxidizers, such as thermal instability and chemical reactivity, or health hazards of gaseous products generated during combustion or decomposition. Dangerous reactions can occur if oxidizers are exposed to fire or other heat sources. If confined, gaseous products generated from oxidizer decomposition can result in overpressure events and explosions. This report and research can be used as part of a full hazard-assessment of oxidizers, including thermal decomposition and reaction to contaminants.

The results in this report do not include an evaluation of oxidizer-containing explosive mixtures, pyrotechnic mixtures, and oxidizers stored in non-combustible vessels or in non-combustible packaging. Recognizing that some oxidizers are packaged in non-combustible packaging, this research and proposed tests and criteria involved combustible test packaging consisting of plastic and corrugated cardboard, which may not be representative of oxidizers in their normal packaging.

Lastly, the proposed tests and criteria assign an oxidizer to a NFPA Class for storage. The NFPA Class is not applicable to and should not be confused with transportation or Packing Group assignment and vice versa. The Department of Transportation (DOT) and United Nations (UN) Packing Group (III, II, I) assignments are different from, and not synonymous with, the NFPA Class (1, 2, 3, 4) assignments for storage.

Background

Recognized hazards of chemical oxidizers are the potential to (1) increase the burning rate of combustible materials; (2) cause spontaneous ignition of combustible materials; (3) decompose rapidly; (4) evolve or emit hazardous gases; (5) undergo self-sustained decomposition which can result in an explosion; and (6) react explosively if mixed with incompatible materials or if involved in an exposure fire[6]. Whether it decomposes and initiates a fire or is involved in an exposure fire, an oxidizer can release an oxidizing gas, in the condensed and/or gaseous phase, that can increase the intensity of a fire compared to normal combustible materials. The degree and/or range of hazards vary and are different for each oxidizer. Storage environment-related combustible materials with which oxidizers come into contact include combustible packaging and pallets.

The loss history of oxidizers includes large fires during transportation and storage. Recent fires involving oxidizers have occurred at waste treatment facilities. Contaminated sodium chlorate, for example, resulted in the destruction of a warehouse at Teris LLC in El Dorado, Arkansas in January 2005.[7] A subsequent fire at an EQ hazardous waste treatment facility in Apex, North Carolina,[8] originated where tablet-form swimming pool treatment chemicals and sodium chlorate oxygen generators were stored.

Solid and liquid oxidizers are available as formulated products and can exist in different product forms. Solid product forms include powder, granular, and compacted solid. Compacted solid oxidizers include pellets, briquettes, pill or disk-shaped tablets of varying diameter, and solid candles (i.e., oxygen generators, emergency road flares). Some oxidizers are neat or pure; some are hydrated or anhydrous; others are formulated. In formulated products, the concentration of the oxidizer constituent can vary. Examples of oxidizers that vary in concentration in commercial formulated products are sodium dichloroisocyanurate dihydrate, trichloroisocyanuric acid, sodium percarbonate, and calcium hypochlorite. Other constituents or additives in oxidizer-containing commercial products may include hydrated salts, inert or non-oxidizers, and/or oxidizing components. The number and concentration of additives in a formulated product also vary.

Some oxidizers are explosive chemicals or explosive precursors. The National Research Council's Committee on Marking, Rendering Inert and Licensing of Explosive Materials identified ammonium nitrate as an explosive chemical, nine oxidizers that could be physically mixed with a fuel to produce an explosive composition, and two liquid oxidizers as precursors requiring chemical reactions.[9] Solid and liquid oxidizers that made the Committee's short list of explosive precursors most likely to be used in bomb-making were ammonium nitrate, sodium nitrate, potassium nitrate, sodium chlorate, potassium chlorate, potassium perchlorate, hydrogen peroxide, and nitric acid. Recently, the Natural Resources Canada (NRCan) *Explosives Act* listed nine chemicals as explosive precursors, eight (six solids and two liquids) of which were oxidizers.[†] The new regulation requires buyers and sellers of restricted components to enroll with NRCan and to comply with security measures where these materials are stored

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[†] Ammonium nitrate (solid, 28-34% nitrogen), hydrogen peroxide (liquid, ≥30%), nitromethane, potassium chlorate, potassium perchlorate, sodium chlorate (solid), nitric acid (liquid, ≥ 68%), potassium nitrate, and sodium nitrate (solid). The non-oxidizer restricted component is liquid nitromethane.

and when transported, including record keeping and identification of customers with materials above threshold quantities.[10]

The fire codes utilize a system for classifying oxidizers based on their potential fire hazard. In the four-class system, oxidizers assigned to Class 1 are least hazardous, while those assigned to Class 4 exhibit the most severe physical hazards (i.e., explosive reaction). NFPA 430 *Code for the Storage of Solid and Liquid Oxidizers* applied to the storage and handling of oxidizers and provided requirements for the safe storage of commercially available strengths of oxidizers based on their Class. NFPA 430 Code was consolidated with other hazardous materials codes into the new NFPA 400 *Hazardous Materials Code*. The definitions of Class 1, Class 2, Class 3 and Class 4 oxidizers and those listed as typical of each Class in the Annex did not change. Class 4 oxidizers are considered high hazard level 1 contents; Class 3 oxidizers are high hazard level 2 or level 1 contents; Class 2 solid and liquid oxidizers are high hazard level 1 contents. The hazard level of Class 3 solid and liquid oxidizers is based on whether they are used or stored in normally closed containers or systems at gauge pressures more or less than 15 psi (103.4 kPa). The maximum allowable quantities (MAQ) of oxidizer per control area are contained in Chapter 5 and are based on the Class and form of oxidizer, whether the material is in storage or use in open and closed systems and the building occupancy. Chapter 6 contains the fundamental requirements for the safe storage, use and handling of hazardous materials in general; for storage when exceeding the MAQ per control area for high hazard level contents; and for use, dispensing and handling in amounts exceeding the MAQ. Specific fire protection requirements for solid and liquid oxidizers in various storage configurations are contained in Chapter 15 and are based on the oxidizer Class. Class specific requirements include limitations on the quantity of material, allowable distances, and sprinkler criteria.

There are well over 90 different solid and liquid oxidizers. The Code's Annex lists twenty-eight "typical" Class 1 oxidizers, forty-three Class 2 oxidizers, and fifteen Class 3 oxidizers. Only five oxidizers are listed as Class 4. In the past, oxidizers were assigned to a Class based on evaluation of available scientific and technical data, experience, historical fires and results of tests by conducted by the Bureau of Mines and GE Research in the 1970s. Ammonium nitrate and organic peroxides are contained in Chapter 11 and Chapter 14 of the *Hazardous Materials Code*, respectively.

Since their establishment in 1973, the NFPA definitions of Class 1, Class 2, Class 3, and Class 4 oxidizers have been subjective and require interpretation. Revisions to the Code also have included changes to the definition of oxidizer as well as the subjective descriptions used to define each Class. Since 2004, oxidizers are assigned to Class 1, Class 2, Class 3 or Class 4 based on the degree to which the oxidizer increases the 'burning rate' of combustible materials with which it comes into contact; however, burning rate is not defined by the Code. The NFPA Code has never had tests or criteria to assess burning rate or for assigning an oxidizer to a Class. On occasion, the Hazardous Chemicals Technical Committee has classified or re-classified specific oxidizers based on fire losses and/or results from reaction-to-fire tests with oxidizers in their intended form and packaging, with and without calorimetry. These tests have included intermediate-scale and pallet-scale forced-ignition/fire exposure tests.

The goals of this project were to 1) define burning rate in terms of fire-test-response characteristics, 2) develop reaction-to-fire tests to quantify the degree to which an oxidizer increases or enhances the burning rate of combustible materials, and 3) develop burning rate criteria to classify oxidizers based on the NFPA definitions of Class 1, Class 2, Class 3 and Class 4 oxidizers.

Significance and Use

The tests and criteria proposed herein provide a technical basis for the classification of oxidizers based on the quantity and duration of energy released as a result of its involvement in a fire. The use of an intermediate-scale fire exposure test method is consistent with the Hazardous Chemicals Technical Committee's preference for real-scale scenarios. The bench-scale screening test designed reduces the need, number, and expense associated with intermediate-scale testing. The data contained in this report also can be used to assess the classification of oxidizers, or formulations containing oxidizers, that differ from their current Class and/or that are not listed in the Code's Annex.

A fire hazard assessment of oxidizers based on burning rate only has limitations. Information on other oxidizer physical hazards (e.g., reactivity, thermal instability) is not provided, nor is information on the toxicity of gaseous products of decomposition and/or combustion. The assessment does not include the potential for explosive reactions or provide information on the behavior of oxidizers in non-combustible packaging or vessels when exposed to fire. It is assumed that the maximum allowable quantities per control area and occupancy and the fire protection strategies for Class 1, Class 2, and Class 3 oxidizers are appropriate for the safe storage of these materials.

Safety

Oxidizers are hazardous materials that pose both physical and health hazards. The safe handling, storage, testing, and disposal of oxidizers and post-test residue require knowledge of and training regarding these hazards, including (but not limited to) the information provided in Materials Safety Data Sheets (MSDS) and product technical information.

Bench-scale screening tests should be performed by experienced laboratory personnel with training in chemical safety and performed in a clean laboratory hood capable of removing gaseous products of combustion and/or decomposition. Intermediate-scale fire exposure testing requires personnel with advanced training and experience in fire safety and fire test methodologies and should not be performed by untrained personnel. Intermediate-scale testing should not be performed without some bench-scale screening tests.

MSDS and product information should be consulted before handling and storing oxidizers prior to testing. Some oxidizers are hygroscopic, toxic, and/or require temperature control. The MSDS provides useful information on the composition and fundamental properties of the material, including decomposition temperature, toxicity, hazardous products of decomposition, and special fire extinguishing, safe handling, and disposal considerations.

<div align="center">

DEFINITIONS

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The following terms are used in this report.

Active Burning Time. Duration (s, min) of burning with flaming combustion, or decomposition with minor flaming combustion, calculated from test data. From bench-scale screening test data, the active burning time is calculated as the time from first measurable mass loss to the time at which 80% of the mixture is consumed and/or decomposed. From intermediate-scale radiant heat flux test data, the active burning time is the width of the curve at one-half the peak radiant heat flux.

Burning Behavior. The complete characterization of a material or mixture's reaction to fire. Burning behavior includes both visual descriptors and test data.

Burning Rate. (1) The mass of solid or liquid fuel consumed per unit time (g/s).[11] (2) The *intensity*, characterized by the quantity of energy released in the form of heat and light or fire, and *time duration* over which the energy is released.

Chemical Heat Release Rate. Heat release rate (kW) calculated from the composition of the combustion gases either by oxygen consumption calorimetry (HRR_{O2} or $\dot{q}_{O_2}$) or carbon dioxide and carbon monoxide generation (HRR_{CO2} or $\dot{q}_{CO_2}$). (see also Heat Release Rate)

Convective Heat Release Rate (HRR_{conv} or $\dot{q}_{conv}$). Heat release rate (kW) estimated from the temperature increase of the combustion gases in the exhaust duct. (see also Heat Release Rate)

Fire-test-response Characteristic[12]**.** A response characteristic of a material, product, or assembly to a prescribed source of heat or flame, under controlled fire conditions; such response characteristics may include, but are not limited to, ease of ignition, flame spread, heat release, mass loss, smoke generation, fire resistance, and toxic potency of smoke.

Formulated Product. A product that contains an oxidizer as one of its constituents, including admixtures. Some oxidizers are not sold in pure form (i.e., lithium hypochlorite, calcium hypochlorite). Formulations include unavoidable by-products and un-reacted raw materials inevitably present in the product and intentionally added diluents and exotherm control agents, such as hydrated salt crystals coarsely blended with the manufactured oxidizer. The MSDS and stereoscopic examination of the material are used to distinguish between a homogeneous material and an admixture of two or more granular solids.

Heat Flux.[12] Heat transfer to a surface per unit area per unit time (kW/m^2-s).

Heat Release.[13] Amount of heat evolved, produced, or released from burning material or combustion of a given weight (J/g) or volume (J/cm^3) of material.

Heat Release Rate (HRR).[12] Measure of fire intensity based on quantity of heat evolved, produced, or released during combustion, usually expressed per unit time (J/s) or per unit quantity of material (J/g). Thermal energy released per unit time by an item during combustion under specified conditions.

Mass Loss. The change in mass of a solid material to gaseous products during combustion or decomposition expressed per unit quantity of material (g/g, %).

Mass Burning Rate.[12] Mass loss per unit time (g/s, kg/min) by materials burning under specified conditions.

Oxidizer. (1) A chemical other than a blasting agent or explosive that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases;[14] (2) Substances (Division 5.1) which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material;[3,15] (3) Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials and, under

some circumstances, can undergo a vigorous self-sustained decomposition due to contamination or heat exposure.[1]

> **Class 1 Oxidizer.** An oxidizer that does not moderately increase the burning rate of combustible materials with which it comes into contact.

> **Class 2 Oxidizer.** An oxidizer that causes a moderate increase in the burning rate of combustible materials with which it comes into contact.

> **Class 3 Oxidizer.** An oxidizer that causes a severe increase in the burning rate of combustible materials with which it comes into contact.

> **Class 4 Oxidizer.** An oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock and that causes a severe increase in the burning rate of combustible materials with which it comes into contact.

Packaging. The intended outer wrapping of the test material, including plastic bottles, bags, corrugated board carton, pails, and fiberboard drums.

Radiant Heat Flux. Energy released from a burning object in the form of convective and radiant heat fluxes transferred to the surface of a gage that absorbs the heat at one surface and transfers the heat in a direction normal to the absorbing surface (kW/m^2).

Screening Test.[12] A fire-response test performed to determine whether a material, product, or assembly (a) exhibits any unusual fire-related characteristics, (b) has certain expected fire-related characteristics, or (c) is capable of being preliminary categorized according to the fire characteristic in question.

Test Packaging. Packaging for solid (granular, tablet or powder) oxidizers during the intermediate-scale fire exposure test consisting of six, high-density polyethylene (HDPE) containers in a double-wall corrugated board carton.

Visual Burning Duration. Duration (s, min) of visible flaming combustion, as measured with a stopwatch.

MATERIALS

Cellulose Powder (Whatman CF11)

Dry, fibrous cellulose powder (Whatman CF11) was used as combustible fuel for bench-scale screening test mixtures. Mean fiber size ranged from 50 to 350 microns.

Cellulose is an organic polymer. Its chemical formula is $(C_6H_{10}O_5)_n$. From the Whatman CF11 product specification sheet, the CF11 cellulose powder is a diethylaminoethyl-derivatised cellulose or cellulose-O-$(CH_2)_2N(C_2H_5)_2$. The chemical structure consists of pyranose rings with hydroxyl- and methoxy-functional groups. Figure 1 shows two stereomicroscope images of the cellulose powder and its FTIR spectrum. On a mass basis, the cellulose powder used contained 49.6% oxygen, 43.9% carbon, 6.2% hydrogen, and 0.16% nitrogen. Table 1 summarizes the properties of cellulose powder from the manufacturer's product specification sheet. The moisture content of cellulose powder was confirmed using an analytical moisture analyzer. Moisture content was reduced by drying in an oven at 108°C for 4 to 5 hours.

Reaction-to-fire test data of dried cellulose powder from combustion-type tests with a Fire Propagation Apparatus are summarized in Table 2. The calculated effective heat of combustion of dried cellulose powder was 19.2±0.4 kJ/g. A literature value for heat of combustion of cellulose is 16.1 kJ/g[16]. For comparison, polyethylene's heat of combustion is 43.3 kJ/g.

TABLE 1. Properties of Whatman CF11 Cellulose Powder (Lot No. 7311083).

Mean particle size (fiber length)	50–350 microns
Moisture content (as-received)	3.86%
Dry density	56 ml per 20 g
Iron (Fe)	2.0 ppm dry weight
Copper (Cu)	0.05 ppm dry weight
Ash	0.012%

TABLE 2. FPA Reaction-to-Fire Test Data of Whatman CF11 Cellulose Powder (30-g)

Moisture content	0.37±0.05 wt%
Peak heat release rate based on carbon dioxide generation	2.10±0.11 kW
Total heat release based on carbon dioxide generation	567±12 kJ
Peak convective heat release rate	0.87±0.08 kW
Total heat release based on gas temperature rise	295±25 kJ
Peak mass loss rate	0.099±0.002 g/s
Percent material consumed	98.2±0.3 wt%
Effective heat of combustion	19.2±0.4 kJ/g
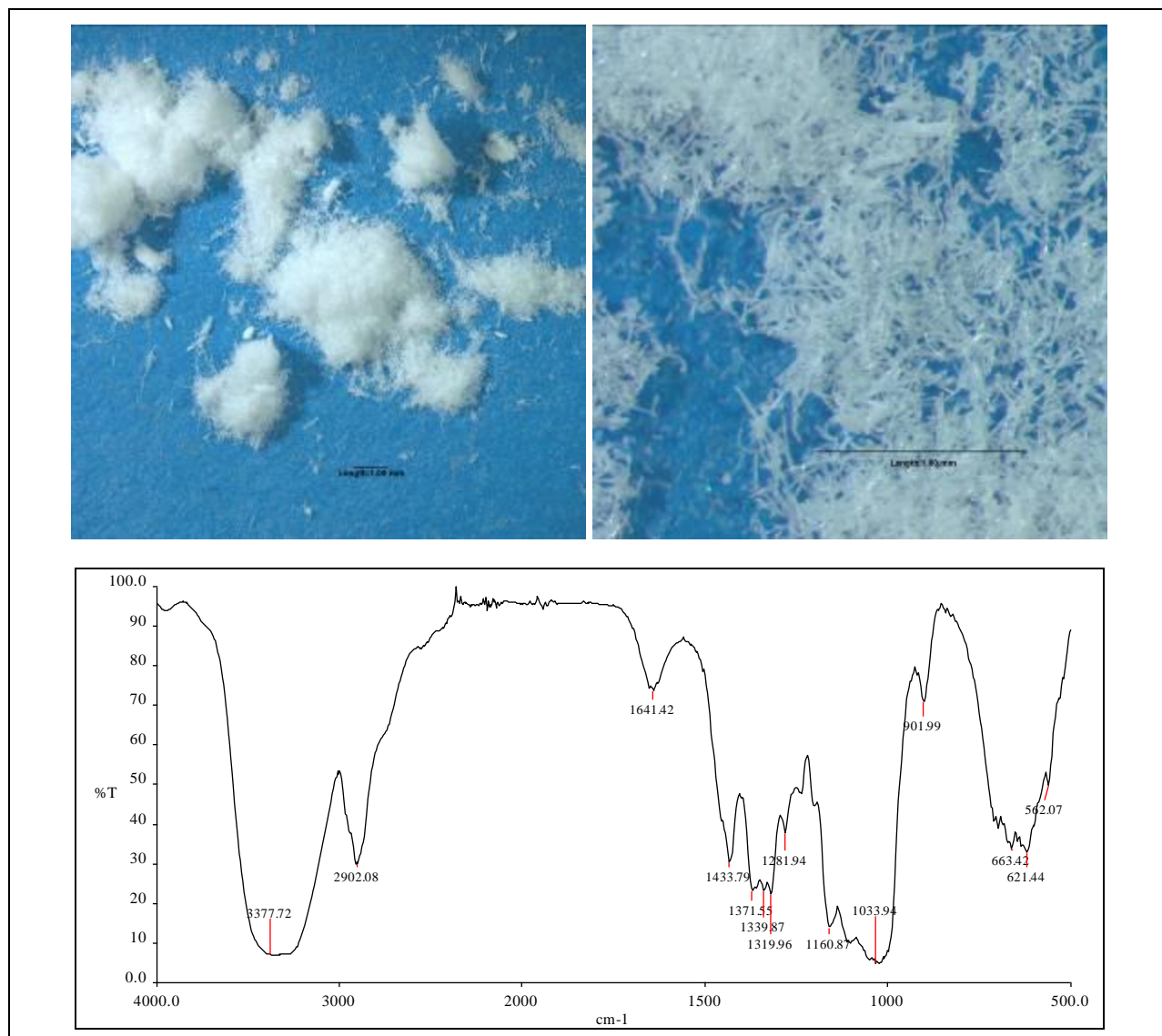
FIGURE 1. Stereomicroscope images (top) and FTIR spectrum of Whatman CF11 cellulose powder (bottom) (Lot No. 7311083).

Combustible Test Packaging Used in Intermediate-Scale Fire Exposure Tests

Oxidizers can be packaged and stored in combustible and non-combustible packaging. Combustible packaging includes plastic thin-film sealed bags in corrugated board cartons, high-density-polyethylene (HDPE) bottles in corrugated board cartons, HDPE pails, and fiberboard drums. HDPE is the most common combustible packaging material used for commercial oxidizers in retail stores (Fig. 2). The size and shape of individual HDPE containers varies. The net weight of material in HDPE bottles ranges from 2 lbs (0.91 kg) to 6 lbs (2.72 kg) and in HDPE pails from 24 lbs (10.9 kg) to 50 lbs (22.7 kg). In storage environments, oxidizers in corrugated board cartons, pails, and fiberboard drums are typically arranged on combustible pallets.

HDPE containers and 1-lb bags in corrugated board cartons and HDPE pails were used as combustible test packaging for the intermediate-scale fire exposure tests. HDPE containers included a 60-ounce (1,774 cm^3) container, an 85-ounce (2,514 cm^3) container, and a 2.5 US gallon (320 ounce, 9,463 cm^3) pail (Fig. 3). The 60-ounce HDPE containers could accommodate 1.8 kg (4 lbs) of material and were used in most tests with crystalline, granular and tablet form oxidizers. The 85-ounce HDPE containers were used in tests with low-density, powder-form calcium peroxide and phenolic resin. The 60-ounce and 85-ounce HDPE containers and HDPE pails were procured from Consolidated Plastics Inc. (Twinsburg, Ohio).

The corrugated board cartons had doubled-wall construction. The cartons were made by JM Packaging-Detroit Tape and Label (Warren, Michigan). The dimensions of the corrugated board carton used to enclose six 60-ounce HDPE containers were 16 in x 10 in x 8 in (40.6 cm x 25.4 cm x 20.3 cm). The dimensions of the corrugated board carton used to enclose six 85-ounce HDPE containers were 16 in x 10 in x 10 in (40.6 cm x 20.3 cm x 20.3 cm). The average mass of the 16 in x 10 in x 8 in doubled-wall carton was 625 grams (1.4 lbs). Figure 4 shows six 60-ounce HDPE containers in a doubled-wall corrugated carton.

The dimensions of the HDPE containers and pails and the dimensions and properties of the carton are summarized in Tables 3 and 4, respectively.

TABLE 3. Dimensions of HDPE Containers and Pail with Lids

Volume Ounce (cm^3)	Overall Height Inch (cm)	Outer Diameter Inch (cm)	Wall Thickness Inch (cm)	Mass (g)
60 (1,774)	6.38 (16.19)	4.81 (12.22)	0.04 (0.10)	99
85 (2,514)	8.50 (21.60)	4.75 (12.06)	0.04 (0.10)	114
320 (9,463)	12.50 (31.75)	9.5 (24.13)	0.08 (0.20)	919

TABLE 4. Properties of Double Wall Corrugated Board Carton

	Bursting Test Pressure (psi)	Min. Combined Weight Facings (lb/ft^2)	Wall thickness in (cm)	Gross weight limit lb (kg)
DW Carton	275	110	0.265 (0.673)	100 (45.4)

FIGURE 2. Commercial oxidizers in combustible packaging.

FIGURE 3. HDPE containers and pail used as combustible test packaging in intermediate-scale fire exposure tests. The 60 ounce HDPE container was used in a majority of the tests.

FIGURE 4. Combustible test packaging consisting of a doubled-wall carton (left) and containing six 60-ounce HDPE containers(right), each of which contained 4 pounds of granular, crystalline, or tablet form common salt or oxidizer.

Inert Material

Sodium chloride (99.5%, NaCl, CAS No. 7647-14-5), or common salt, is a readily available inorganic solid that does not contribute to the burning rate of combustible materials. Sodium chloride is sold in fine to coarse granular or crystalline form, as pellets, as compacted spools or tablets, and as large blocks (50 lbs) that can be machined to tablets of different size and shape.

Organic Phenolic Resin Powder

Phenolic resin powder is an organic material with a high surface area that does not readily ignite or burn or cause a significant increase in the burning rate of combustible packaging. Figure 5 contains stereomicroscope images and the FTIR spectrum of phenolic resin powder.
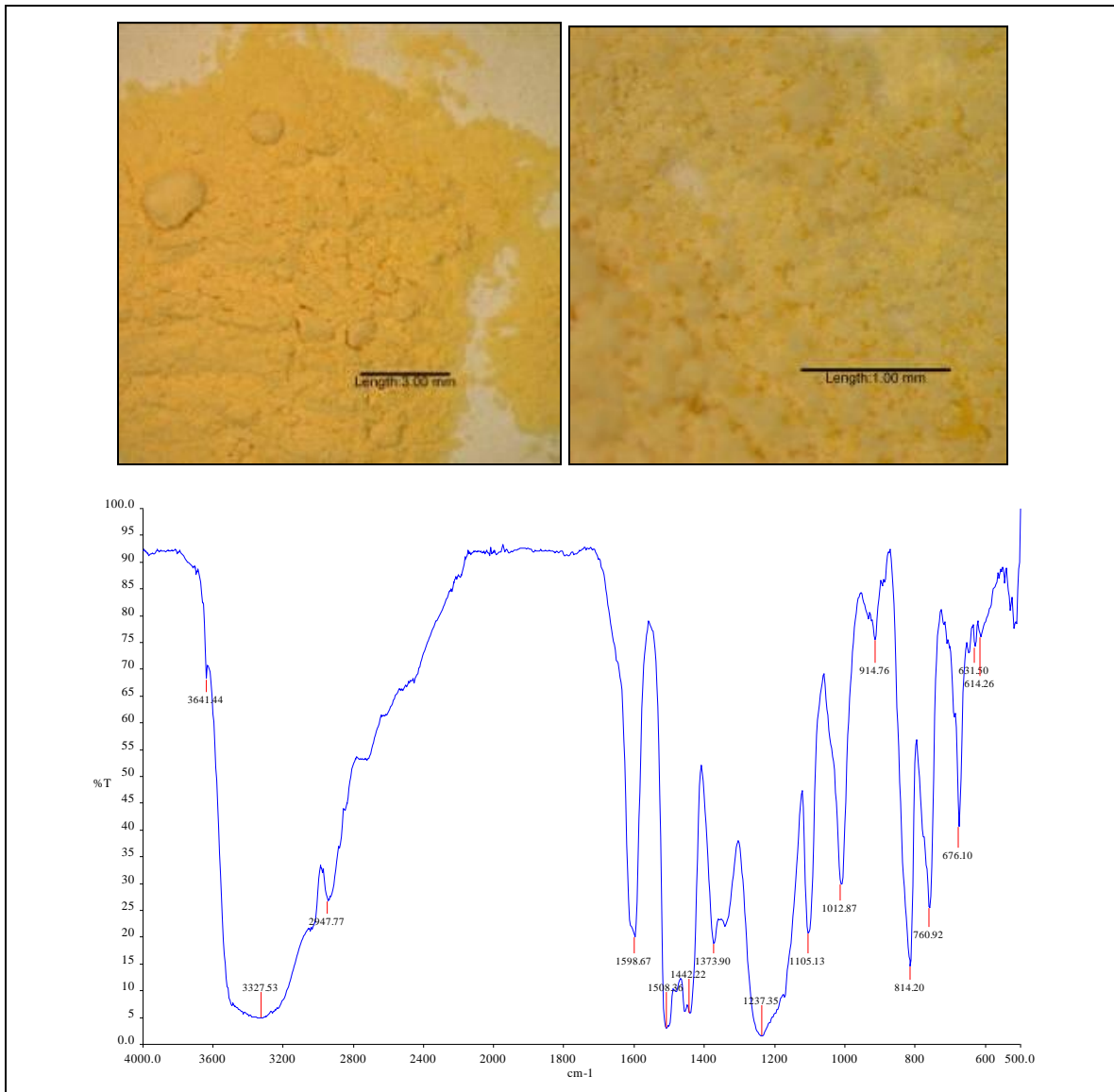
FIGURE 5. Stereomicroscope images (top) and FTIR spectrum (bottom) of phenolic resin powder.

Chemical Oxidizers

The oxidizers listed in NFPA 400 Annex G (formerly NFPA 430 Annex B) as typical Class 1, Class 2, Class 3, and Class 4 are reproduced in Appendix 1. In Appendix 1, the solid oxidizers tested at some level in this research project are highlighted yellow, and the liquids are highlighted blue. The solid and liquid oxidizers are further described in Table 5, which includes each oxidizer's chemical formula, CAS number, purity or concentration, physical form, and, if applicable, current NFPA Class. Appendix 2 contains a table of the same oxidizers listed with their current NFPA Class and UN hazard class, number, and packing group.

Table 5 lists eleven current Class 1 solid oxidizers, three current Class 2 solid oxidizers, four current Class 3 solid oxidizers, and two current Class 2 liquid oxidizers. Only two liquid oxidizers were included in the research project: hydrogen peroxide (50%) and sodium permanganate (20–40%).

Two solid oxidizers in Table 5 are not listed in the Code's annex: sodium nitrate and potassium peroxymonosulfate or potassium monopersulfate ($KHSO_5$). Potassium monopersulfate is a component of a triple salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) that contains 4.5–5.2% active oxygen. In pure form, triple salt is 49.5% potassium monopersulfate. Commercial products contain about 45% potassium monopersulfate, being a slightly diluted or partially decomposed triple salt. Commercial products include denture cleaners, swimming pool/spa oxidizers, and laundry bleach. Triple salt and diluted products are labeled corrosive solids.

According to the Code's annex, "all inorganic nitrates and nitrites are Class 1 unless otherwise classified." This includes sodium nitrate ($NaNO_3$), which is one of eight oxidizers identified by the NRCan *Explosives Act* as a restricted component. It is also one of three oxidizers evaluated as part of the IGUS Oxidizing Substances Ad Hoc Working Group's UN O.1 Round Robin Test.[†] The results of the round robin testing are immediately applicable to the current research.

[†]Sodium nitrate was evaluated because it is 'supposed to be a medium oxidizer of Packing Group II in consideration of its oxidizing properties, although listed officially as a weak oxidizer of Packing Group III (PG III UN1498)'.

TABLE 5. Description of Oxidizers Included in the Test Plan

MATERIAL	Chemical Formula	CAS No.	Purity/ Concentration	Physical Form	Current NFPA Class
SOLID OXIDIZERS					
Sodium nitrate	$NaNO_3$	7631-99-4	100%	Crystalline	NC
Potassium monopersulfate	$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	10058-23-8	45% $KHSO_5$ or ~90% $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	Crystalline	NC
Barium nitrate	$Ba(NO_3)_2$	10022-31-8	99%	Crystalline	1
Magnesium peroxide complex	$MgO_2 \cdot MgO$	1335-26-8	24-28% MgO_2 13.7% Avail oxygen	Powder	1
Sodium persulfate	$Na_2S_2O_8$	7775-27-1	99%	Crystalline	1
Sodium dichloroisocyanurate dihydrate	$NaCl_2(NCO)_3 \cdot 2H_2O$	51580-86-0	99% w/ 55% Avail. Cl_2	Granular	1
Trichloroisocyanuric acid	$Cl_3(NCO)_3$	87-90-1	99% w/ 90% Avail. Cl_2	Granular/ Tablets	1
Lithium hypochlorite	$LiOCl$	13840-33-0	29wt% w/ 35% Avail Cl_2, 8.8% Avail Oxygen	Granular	1
Calcium peroxide	CaO_2 w/ $Ca(OH)_2$	1305-79-9	75%	Powder	1
Calcium peroxide	CaO_2 w/ $CaCO_3$	1305-79-9	75%	Powder	1
Sodium percarbonate	$2Na_2CO_3 \cdot 3H_2O_2$	15630-89-4	65%, 99%	Granular	1
Sodium perborate monohydrate	$NaBO_3 \cdot H_2O$	10332-33-9	>96%	Granular	1
70:30 Calcium hypochlorite: magnesium sulfate heptahydrate†	$Ca(OCl)_2 : MgSO_4 \cdot 7H_2O$	7778-54-3, 10034-99-8	50.87% Avail Cl_2, 22% H_2O	Granular	1
Calcium hypochlorite: sodium chloride	$Ca(OCl)_2 : NaCl$	7778-54-3	33% and 48% Avail Cl_2	Granular	2
Potassium permanganate	$KMnO_4$	7722-64-7	>97.5%	Crystalline	2
Potassium perchlorate	$KClO_4$	7778-74-7	99+%	Crystalline	2
Potassium bromate	$KBrO_3$	7758-01-2	99.8%	Crystalline	3
Calcium hypochlorite	$Ca(OCl)_2$	7778-54-3	72.68% Avail Cl_2, 5.7% H_2O	Granular/ Briquettes	3
Calcium hypochlorite	$Ca(OCl)_2$	7778-54-3	78.6% Avail Cl_2, 11.2% H_2O	Granular	3
Sodium chlorate	$NaClO_3$	7775-09-9	99+%	Crystalline	3
LIQUID OXIDIZERS					
Hydrogen peroxide	H_2O_2	7722-84-1	50%	Clear liquid	2
Sodium permanganate	$NaMnO_4$	10101-50-5	20-40%	Dark liquid	2

NC= Not currently Classed in NFPA 400 Annex G.

†Formulated 70:30 calcium hypochlorite:magnesium sulfate heptahydrate is an intentional blend of 73% calcium hypochlorite (5.6% water) and an additional diluent, magnesium sulfate heptahydrate (51wt% water) that acts as an exotherm control agent. The calculated percent available chlorine and moisture content of the admixture are reported in the Table.

The bench-scale screening test, the FPA combustion-type test, single container wood crib fire exposure test, intermediate-scale fire exposure test, and ad hoc tests with liquid oxidizers, using representative photographs are summarized below with references to appendices containing more detailed descriptions. The results and analysis of test data from the intermediate-scale, bench-scale, FPA, single-container, and ad hoc tests with liquid oxidizers are discussed in the subsequent sections.

Materials Characterization

Before each test with a new material, the MSDS was reviewed and basic information regarding the material was recorded. Additional material characterizations were performed, including particle morphology, particle size distribution, bulk density and solid-state Fourier Transform Infrared (FTIR) spectroscopy.

Bench-Scale Screening Test for Granular Solid Oxidizers

The bench-scale screening tests were done inside a clean laboratory hood. Thirty-gram (30 gram) mixtures of the oxidizer, with the as-received particle size and size distribution, and dried cellulose powder in three ratios (1:1, 4:1, 9:1 by mass) were prepared and exposed to a glowing 150±7 Watt Nichrome wire ignition source. The forced ignition of the oxidizer-cellulose powder mixtures was done on a calibrated, laboratory balance with time-stamped data output to a data acquisition system. The balance's weighing surface was protected with high-temperature, low-thermal conductivity ceramic fiberboard. The cellulose powder was dried in a laboratory oven, and its moisture content monitored with a moisture analyzer.

For a typical test, the prescribed amounts of oxidizer and cellulose powder were weighed and combined in a clean polyethylene container, thoroughly mixed, and then transferred into a funnel with the stem opening sealed. Using card stock paper, the funnel with mixture was inverted over the Nichrome wire on the lab balance. Three K-type thermocouples were positioned at 7.6 cm (3 inches), 15.2 cm (6 inches), and 22.8 cm (9 inches) above and centered over the test platform and pile (Fig. 6). A fourth K-type thermocouple monitored the ambient temperature. After transferring the material to the balance, the balance display was tared to zero, and data acquisition was initiated. Mass loss and temperature data were collected at 0.2 second to 1 second intervals depending on how fast or slow the mixture ignited and burned.

At the start of a trial, the Nichrome wire under the pile was energized, and a stopwatch activated. Data were collected until spreading discoloration or flaming combustion ceased. When the last small or intermittent flame at the pile went out, the data acquisition was stopped. If the mixture did not ignite, the wire was left energized and the mixture observed for 5 minutes. A test series included five trials each with 1:1 and 4:1 oxidizer:cellulose powder mixtures. Oxidizer-rich (9:1) mixtures also were prepared and tested under the same conditions for some oxidizers. Figure 7 is a representative photograph before and during a screening test.

The time at which the Nichrome wire opened, if at all, was recorded. Other observations noted during each trial were (1) ignition propensity, (2) rate of flame spread over pile, (3) flame color, (4) approximate peak flame height, (5) clarity of endpoint, (6) phase change, and (7) evolution and color of gaseous products. After each test, the Nichrome wire was released from the terminal block, and the test residue and test platform were removed. When cool, the post-test residue was weighed and recorded. Data collected and calculated from these tests are

summarized in Table 6. At a minimum, one representative trial of each oxidizer-fuel mixture was documented with still photographs and a video recording.

Detailed descriptions and photographs of the instrumentation, test set-up, calibration procedures, methodology, test sequence, data reduction, analysis and flow diagram with criteria are contained in Appendix 3.
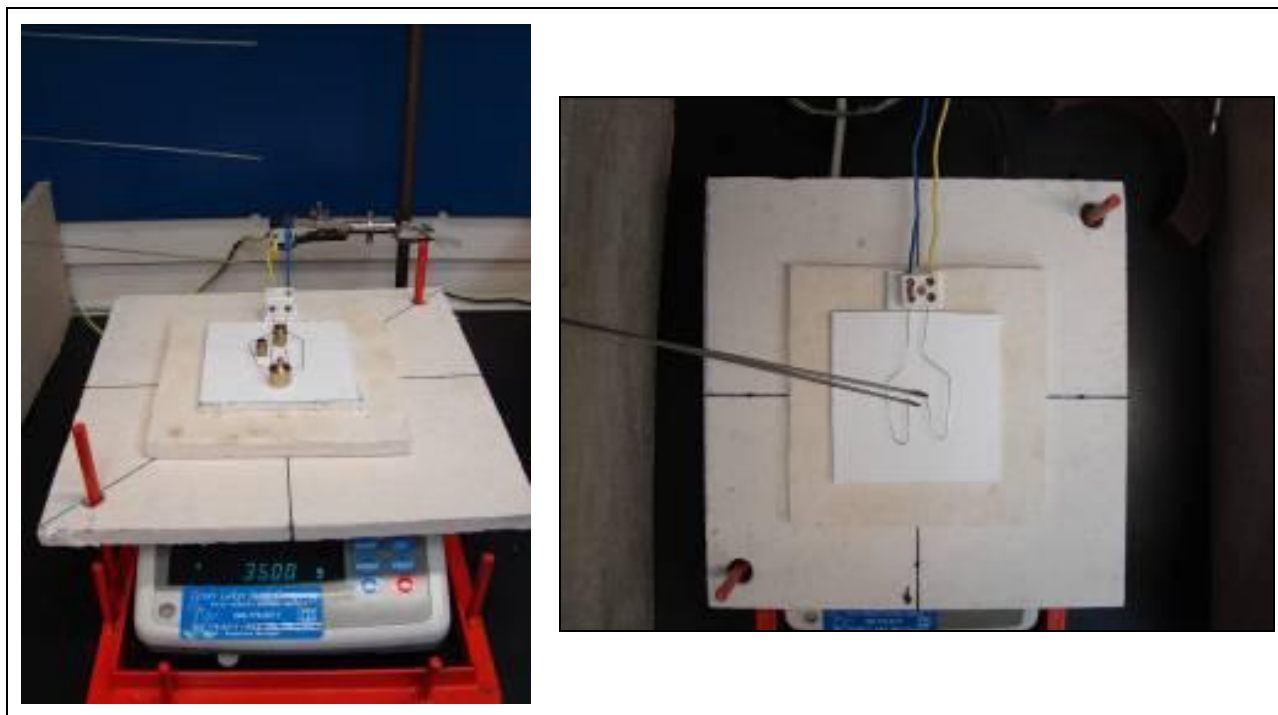
FIGURE 6. Overview of the bench-scale screening test set-up showing the laboratory balance with ceramic board protection materials, thermocouples above the test platform and Nichrome wire.
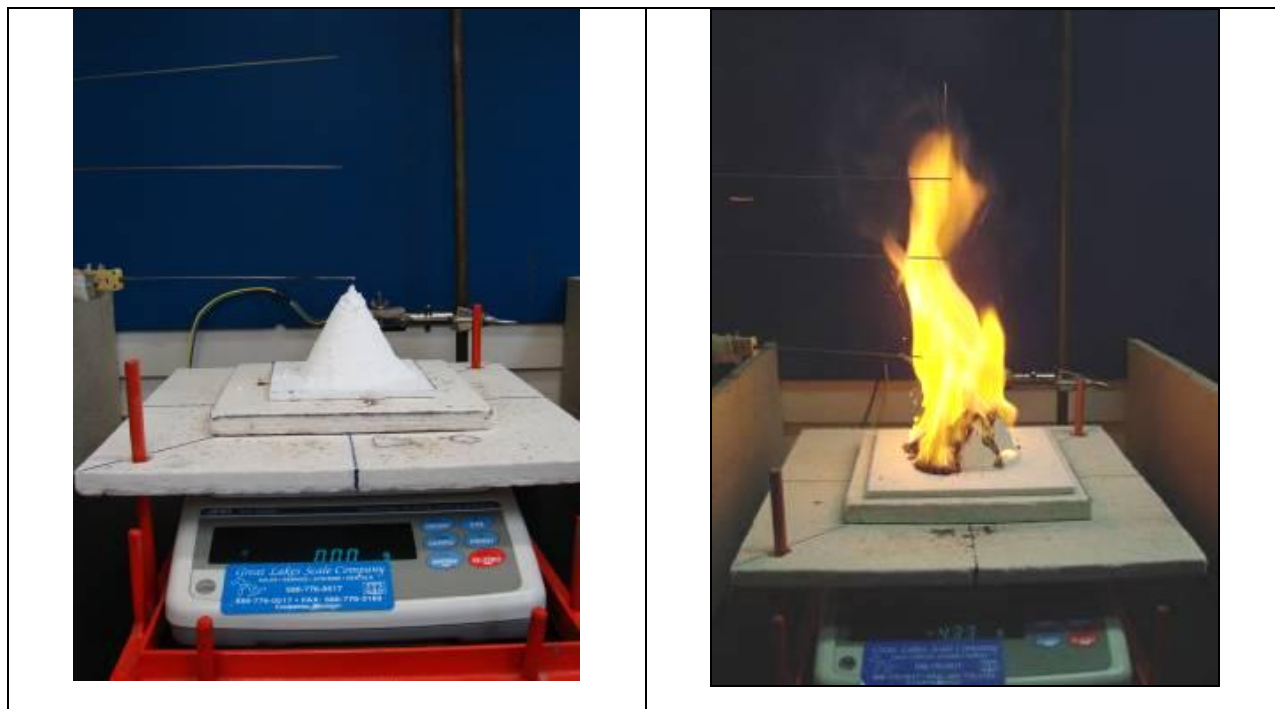
FIGURE 7. Pile of oxidizer-cellulose powder mixture on the protected lab balance before ignition (left) and during combustion (right).

TABLE 6. Bench-Scale Screening Test Data Recorded and Calculated for Each Mixture

Concentration of oxidizer (source of information)	%
Test mixture mass ratio with dry CF11 (Lot No.)	1:1, 4:1 or 9:1
Trial number	
Lab temperature	degree C
Lab relative humidity	%
Initial mass of oxidizer or formulated product	g
Initial mass of cellulose powder	g
Data collection interval	s
Power to Nichrome wire	Watts
Time igniter wire opens	s
Time at end of visible flaming combustion or spreading discoloration	s
Mass of post test residue	g
Video record	
Visual observations	
CALCULATED TEST DATA	
Mass loss rate from 20% to 80% consumed	g/s
Active burning time from first measurable mass loss to 80% consumed	s
Peak temperature at 6-inches above the test platform	degree C
Percent material consumed	%

Single Container Fire Exposure Test

An ad-hoc fire exposure test was developed to compare and evaluate the burning behavior of granular and tablet form sodium chloride (NaCl) and oxidizers. A single container (60-ounce HDPE) with ~2-lbs of material was exposed to a small wood crib fire. The wood crib was constructed with three 8-in x ¾-in x ¾-in and four 4-in x ¾-in x ¾-in wood pieces in a steel pan lined with half-inch thick drywall. The HDPE container with the test material was positioned on top of the small wood crib. Two isopropyl alcohol soaked cotton igniters were positioned under the wood crib in front of the HDPE container. Figure 8 shows an overview of the test set up. Single-container fire exposure tests were documented with video recordings.
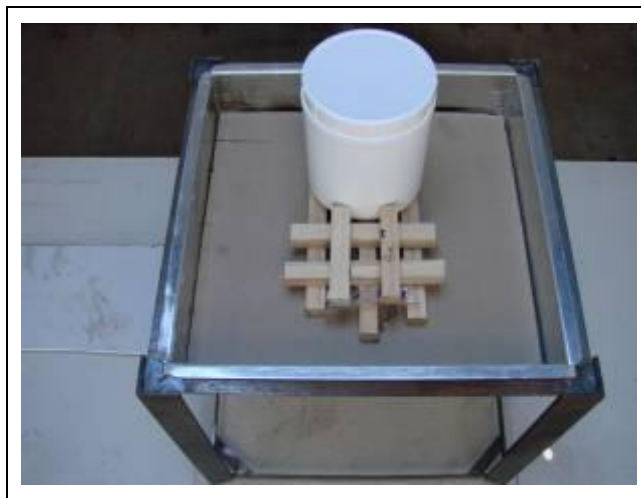
FIGURE 8. Single container wood crib fire exposure test set-up.

Fire Propagation Apparatus (FPA) Combustion-type Tests

Thirty-gram (30 gram) and fifteen-gram (15 gram) mixtures of cellulose powder, sodium chloride-cellulose powder, and 1:1, 4:1 and 9:1 oxidizer-cellulose powder were ignited and burned using the Fire Propagation Apparatus (FPA) at FM Global using the same general procedures as the bench-scale screening test. All FPA tests were documented with photographs and video recordings. An overview of the FPA with a vertical exhaust collection duct is shown in Figure 9.

The moisture content of cellulose powder (CF11) was measured using a moisture analyzer. The sodium chloride (NaCl)-cellulose powder and oxidizer-cellulose powder mixtures were prepared immediately before each test. After thorough mixing in a clean HDPE container, mixtures (30 grams, 15 grams) were transferred to a funnel and then inverted over a Nichrome wire on a test platform centered on an electronic load cell under an exhaust collection hood. A Kaowool ring placed on the test platform around the pile prevented spillover and loss of material during combustion. The ring was open in the area of and did not contact the Nichrome wire. After transferring the material to the test platform, a quartz tube was positioned around the aluminum support cylinder. A close-up of the test platform and Nichrome wire before and after the addition of cellulose powder (30 grams) are shown in Figure 10.

The test platform, wire, and ceramic terminal block were enclosed inside the quartz tube that extended from the test platform to the opening of the hood. The height of the brass ring of the quartz tube assembly was 43.2 cm (17 inches) from the test platform, which served as a fixed distance for estimating the flame height during combustion. The distance from the test platform to the orifice at the opening of the exhaust collection duct was 96.5 cm (38 inches). Make-up air (200 liters per minute) was introduced at the base of the test platform, resulting in forced convection conditions. The gas analyzers were calibrated with carbon monoxide and carbon dioxide calibration gases and nitrogen at the start of each day of testing. The desiccant used to remove moisture from the combustion gases before entering the gas analyzers was exchanged, as required.

At the start of each test, a 30-second baseline was established. The Nichrome wire was then energized at the variable power supply to dissipate 150±7 Watts. Data were collected at 1 second intervals. A stopwatch was activated when the wire was energized. Observations were recorded during each test, the duration of visible flaming combustion, and the time when the Nichrome wire opened, if at all. Data collection continued for 30 seconds after the end of visible flaming combustion. At the conclusion of each test, the test platform and post-test residue were moved to a laboratory hood. When cool, the mass of the post-test residue was recorded. New Nichrome wire and test platforms were used for each test. Heat release rates were calculated using the measured combustion gas temperature and composition with equations in ASTM E 2058.[4]

FIGURE 9. Overview of the FPA at FM Global.

FIGURE 10. Photographs showing modified combustion-type test set up before and after addition of 30g pile of oxidizer-cellulose powder.

Intermediate-Scale Fire Exposure Test

Thirty-two intermediate-scale fire exposure tests were performed at Southwest Research Institute (SwRI, San Antonio, Texas). The heat release rate, radiant heat flux, mass loss rate, and temperature profiles of empty test packaging, packaged sodium chloride, similarly packaged phenolic resin powder and granular and tablet-form solid oxidizers exposed to an external fire were collected. For most tests, the mass of test material (24 pounds, 10.9 kg) and packaging (six 60 ounce HDPE containers in a doubled-walled carton) were identical. The sodium chloride and oxidizers in combustible test packaging were centered on a drywall-lined table and inside the opening of a U-shaped propane-fueled burner and ignited under a calibrated 2 MW hood instrumented in accordance with ASTM E 2067. The average chemical heat release rate of the burner was 38±3 kW.[‡] The hood and duct were located inside a

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[‡] For a 38-kW fire and using propane's effective heat of combustion (46.4 kJ/g), the mass flow rate of propane to the burner was 0.82g/s.

temperature-controlled burn facility. The temperature and relative humidity during the tests were 71°±4°F and 50±10%, respectively. The hood was calibrated with a propane burner before and after the series of intermediate-scale burn tests. The calibration burn results showed that the instrumentation in the hood was within 6% for 100 and 300 kW fires.

Prior to testing, the oxidizer was transferred, in a laboratory hood, from its as-received packaging[§] into the test packaging. During this transfer, a representative sample was collected in labeled 4 ounce glass jars with Teflon-lined lids. Most tests were performed with the oxidizer in the test packaging consisting of six HDPE containers each containing 4 pounds of the oxidizer, enclosed in a doubled-wall carton. Three tests were performed using combustible packaging consisted of twenty-four bags each containing 1 pound of material in a doubled-wall carton; 6 tests involved fire exposure of one or two 2.5 US gallon HDPE pails each containing 24 pounds of test material. The initial mass of the test packaging and oxidizer was recorded.

Data were collected in the exhaust collection duct as well as on the floor at/near the packaged test material. The design and instrumentation of the exhaust system, measurements, and mass flow rate and heat release rate calculations are described in ASTM E 2067. The exhaust collection duct included thermocouples for the measurement of gas temperatures, gas sampling probes, and a light source and target for smoke obscuration. An additional gas sampling probe was inserted in the duct for time-resolved analysis using a heated gas cell and FTIR. The maximum volume flow rate of the exhaust collection hood was 4 m^3/s. At the location of the test material under the hood, mass loss was measured with an electronic load cell. The incident radiant heat flux was measured at two water-cooled Schmidt-Boelter heat flux transducers located at a fixed distance from the test packaging. Temperature was measured using a high-temperature pyrometer and four K-type thermocouples; the thermocouples were located on the exterior and inside the packaging.

A 2 minute baseline was collected at the start of a test. The burner was ignited at 2 minutes and remained on for the duration of the test, after the observed active burning of the test material and for a sufficient duration to establish baseline burner values. The duration of a test ranged from 12–20 minutes. Each test was documented with two digital video cameras and a FLIR thermal imaging video camera. One video camera provided an overview. The second camera provided a close-up view of the oxidizer in its test packaging. Photographs were taken of the test packaging with oxidizer before, during, and after each test.

Figure 11 is a schematic overview of the test set-up under the exhaust collection hood. Figures 12 and 13 are photographs of the test set-up and during a test with an oxidizer, respectively. Figure 14 shows a thermal image captured during a test with an oxidizer. Appendix 4 contains detailed descriptions of the intermediate-scale fire exposure test set up with drawings, photographs, locations of the instrumentation, methodology, heat release and smoke generation rate equations and representative data profiles.

[§] With the exception of potassium perchlorate, which was received in a 5 gallon DOT-approved metal pail, the oxidizer test materials were received in combustible packaging. The combustible packaging included 1 pound bags in corrugated board cartons, HDPE pails, and plastic bags in fiberboard drums.
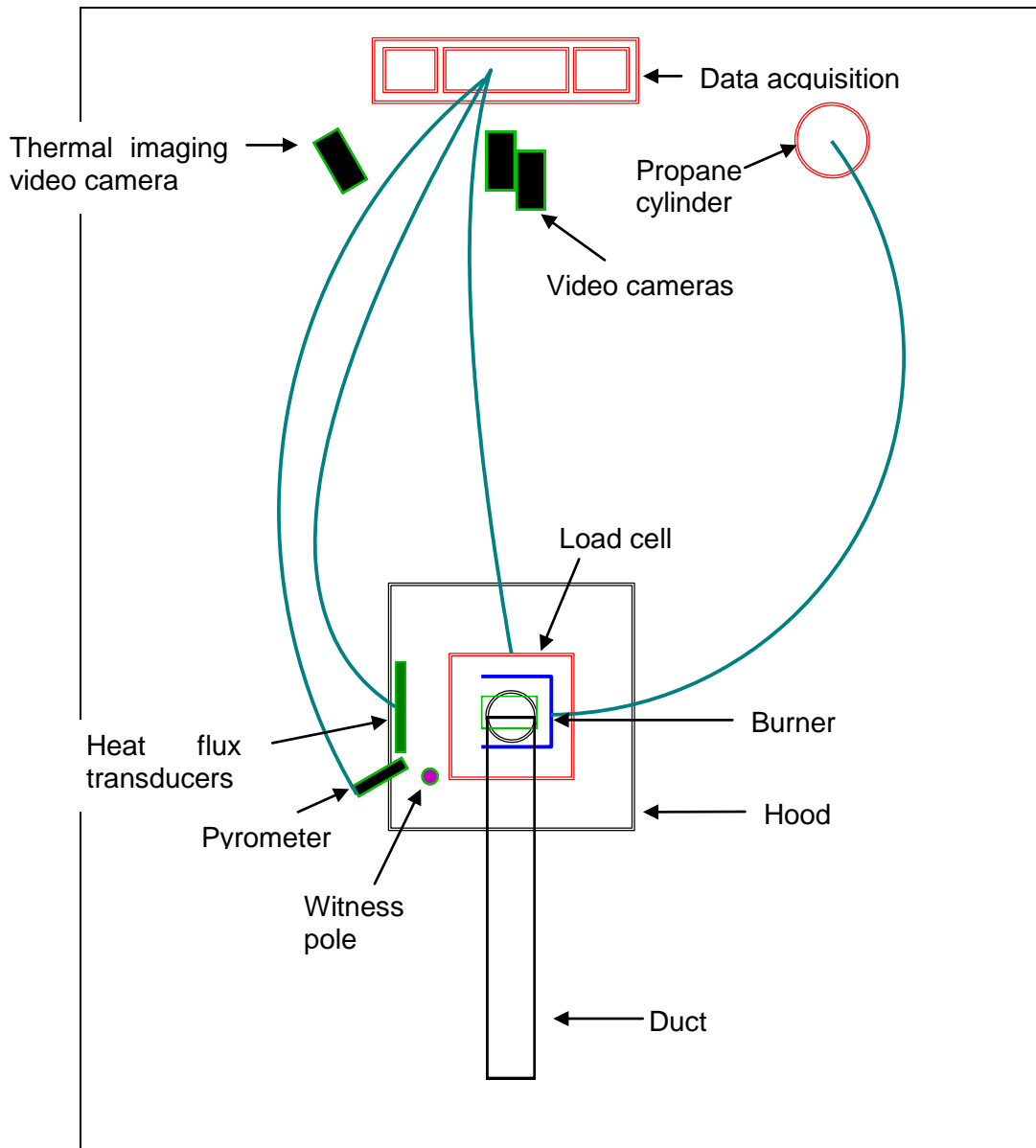
FIGURE 11. Plan view schematic drawing showing the intermediate-scale fire exposure test set-up, identification and location of instrumentation (see Appendix 4).

FIGURE 12. Photograph of the intermediate-scale fire exposure test set up under a 2MW hood.

FIGURE 13. Photograph during fire exposure test with a packaged oxidizer.
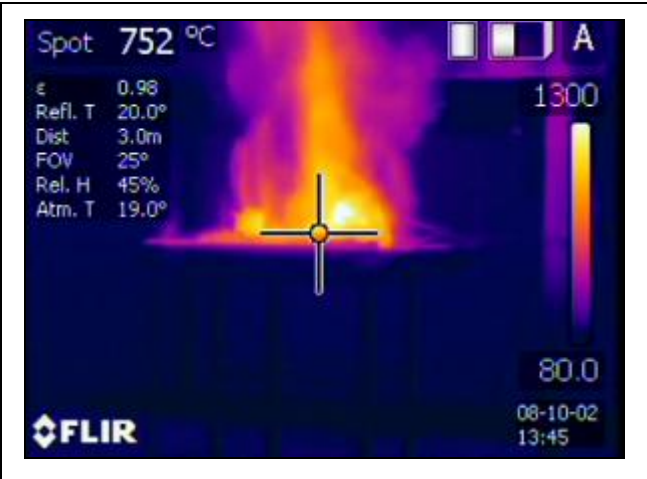
FIGURE 14. Thermal image during a fire exposure test with a packaged oxidizer.

Liquid Oxidizers

Two liquid oxidizers were subjected to a series of ad hoc bench-scale tests. The liquid, as received, was exposed on a glass rod to a Bunsen burner flame for a visual indication of enhanced burning in comparison to a glass rod wetted with water. Next, a sample of liquid was drawn into a plastic pipette (7 mL). The pipette was inverted to pool the liquid inside the plastic bulb. The stem of the plastic pipette was cut just above the bulb with the liquid and then ignited with a small flame. The burning plastic was observed for evidence of increased burning. Next, a sample of the liquid was added dropwise to dried cellulose powder in a dish at room temperature. The mixture was then exposed to a small flame. Finally, a thin film of the liquid was applied to cellulose filter paper at room temperature and observed for 30 minutes for evidence of spontaneous ignition.

Liquid oxidizers were not tested at the intermediate-scale.

MATERIALS - TEST MATRIX

Twenty oxidizers or oxidizer-containing commercial products were evaluated at some level in this project. Over 225 bench-scale screening tests were performed with as-received cellulose powder, dried cellulose powder, sodium chloride (NaCl)-cellulose powder mixtures, and pure and formulated oxidizers mixed with dried cellulose powder. Fifty-nine combustion-type tests using the FPA (cellulose powder, sodium chloride (NaCl)-cellulose powder, and 12 different oxidizers) were performed. Thirty-two intermediate-scale tests were conducted with empty packaging, packaged sodium chloride (NaCl), and fourteen oxidizers in combustible test packaging.

Table 7 provides a matrix of the materials evaluated at the bench-scale, using the FPA, in single containers exposed to a small wood crib fire, and at the intermediate-scale.

TABLE 7. Material-Test Matrix (X indicates testing that was done).

Material	Physical Form	Bench-Scale Screening Test	FPA Combustion Type Test	Single Container Wood Crib Fire Exposure	Intermediate-Scale Fire Exposure
Cellulose Powder	Powder	X	X		
Sodium Chloride	Crystalline	X	X	X	X
Sodium Chloride	Tablets			X	X
Phenolic Resin	Powder				X
Barium nitrate	Crystalline	X	X		
Magnesium peroxide complex	Powder	X			
Sodium persulfate	Crystalline	X	X		X
Sodium dichloroisocyanurate, dihydrate	Granular	X	X		X
Trichloroisocyanuric acid	Granular	X	X		X
Trichloroisocyanuric acid	Tablets				X
Lithium hypochlorite (29%)	Granular	X	X		
Calcium peroxide (75%) with calcium hydroxide	Powder				X
Calcium peroxide (75%) with calcium carbonate	Powder	X	X		
Sodium nitrate	Crystalline	X			
Sodium perborate monohydrate	Granular	X			
Sodium percarbonate (99%)	Granular	X			X
Sodium percarbonate (65%)	Granular				X
Potassium monopersulfate (45% $KHSO_5$ or ~90% $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$)	Crystalline	X			X
Formulated potassium monopersulfate (<45% $KHSO_5$ or <90% $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$)	Crystalline				X
Calcium hypochlorite: magnesium sulfate heptahydrate (70:30)	Granular	X	X		X
1:1 Calcium hypochlorite: sodium chloride admixture (33% Available chlorine)	Granular	X	X		X
2:1 Calcium hypochlorite: sodium chloride admixture (48% Available chlorine)	Granular	X	X		X
Potassium bromate	Crystalline	X			
Potassium permanganate	Crystalline	X	X		X
Potassium perchlorate	Crystalline	X	X		X
Calcium hypochlorite (72.68% Available chlorine, 5.7% water;78.6% Available chlorine, 11.2% water)	Granular	X	X	X	X
Calcium hypochlorite (72.68% Available chlorine, 5.7% water)	Briquettes			X	X
Sodium chlorate	Crystalline	X			

The key physical indicators of burning rate from the intermediate-scale test were peak convective heat release rate and the burning time calculated from the radiant heat flux profile of the packaged test material (i.e., less the burner).

The key physical indicators of burning rate from the screening test were mass loss rate and burning time calculated from the mass data. Temperature and flame height data from the bench-scale tests were secondary indicators used to distinguish between weak oxidizers, strong oxidizers, and oxidizers that principally decompose. These values showed a range consistent with the range in observed burning behavior. The same behavior for the various oxidizer-cellulose powder mixtures subject to ignition by a glowing wire during the screening tests was observed during tests with the FPA. The FPA provided additional combustion gas and calorimetric data of the various mixtures that substantiated and defined the attributes of the bench-scale screening test.

Intermediate-Scale Fire Exposure Test Results

Table 8 summarizes the intermediate-scale fire exposure test data with empty test packaging, five tests with packaged sodium chloride, one test with phenolic resin powder, and 14 different oxidizers. The data are sub-categorized by the quantity of material tested. *The test material's peak heat release rate and peak radiant heat flux are reported; the contributions from the burner were subtracted.* The full SwRI report of results from the intermediate-scale fire exposure testing is available on request from the Foundation.

TABLE 8. Intermediate-Scale Fire Exposure Test Data

Material	Packaging (See note at bottom of table)	Initial Total Mass	Peak HRR_{conv}	Peak HRR_{CO2}	Peak Radiant Heat Flux (Upper Sensor)	Peak Radiant Heat Flux (Lower sensor)	Active Burning Time	Mass loss rate	Mass loss	Peak Surface Temp.	Peak Temp. at Bottom	Peak Temp. Inside Pkg.
		kg	kW	kW	kW/m^2	kW/m^2	s	kg/min	%	C	C	C
Test packaging (Empty)	Carton1	1.22	53	73	3.09	3.15	415	0.13	100	670	712	798
12-lbs (5.45- kg) Net Weight Packaged Material												
Potassium perchlorate (99%)	Carton1	6.38	194	402	11.55	12.53	26	2.66	55	897	1,145	877
	Carton1	6.71	152	334	8.64	7.79	50	2.21	57	935	992	1,317
	Carton1	6.71	195	nr	13.64	11.9	34	3.14	59	1,168	nr	nr
24-lbs (10.8 kg) Net Weight Packaged Material												
Sodium chloride (granular)	Pail	11.79	20	28	0.65	0.54	nd	nd	5	382	75	254
Sodium chloride (tablet)	Carton1	10.37	21	49	0.55	0.42	nd	nd	10	538	323	496
Sodium chloride (granular)	Carton1	12.11	31	67	0.36	0.6	nd	nd	7	455	62	74
	Carton2	11.68	44	90	1.34	1.7	315	0.11	8	652	26	32
Phenolic resin (powder)	Carton 1	9.60	60	94	1.71	2.25	165	0.15	28	611	455	912
Trichlor (3 inch tablets)	Carton1	12.14	38	101	1.66	1.97	230	0.42	22	655	108	531
Trichlor (1 inch tablets)	Carton1	12.27	39	86	1.51	1.63	320	0.36	36	618	101	812
Sodium dichlor dihydrate	Pail	11.86	39	94	1.75	1.93	584	0.34	57	434	313	822
	Carton1	12.12	49	95	0.99	1.22	350	0.42	64	420	35	664
70:30 Cal hypo w/ mag sulfate heptahydrate	Carton1	11.75	45	61	1.47	1.93	180	0.22	15	560	40	613
Trichlor (granular)	Carton1	12.14	55	92	2.28	2.34	208	0.43	35	589	66	432
Formulated Potassium monopersulfate (<45% $KHSO_5$ or <90% triple salt)	Carton1	12.13	58	110	1.99	2.71	180	0.31	18	650	67	362
Sodium percarbonate (65%)	Carton 1	11.96	66	120	2.33	2.61	234	0.37	20	645	402	865
Potassium monopersulfate ((45% $KHSO_5$ or ~90% triple salt)	Carton1	12.13	86	153	2.64	3.15	120	0.56	19	670	289	870
Sodium percarbonate	Carton1	12.10	92	176	4.13	5.2	95	0.82	35	722	518	940
Sodium persulfate	Carton1	12.20	115	228	3.47	4.57	110	0.83	22	630	220	740
Calcium peroxide (75%)	Carton1	11.93	127	219	3.97	5.53	116	0.65	25	773	219	1,012
1:1 Calcium hypo-Sodium chloride	Carton1	11.87	131	248	6.15	7.31	72	0.81	21	753	535	659
	Pail	11.54	149	246	10.74	11.21	80	nr	nr	741	631	979
	Carton2	11.66	164	545	6.74	8.14	30	2.56	21	793	707	740
2:1 Calcium hypo-Sodium chloride	Carton1	11.86	203	356	9.88	12.7	52	1.46	24	859	406	733
Potassium permanganate (>97.5%)	Carton1	12.18	274	571	11.46	14.46	56	2.06	34	879	838	1,175
2:1 Calcium hypo-Sodium chloride	Carton2	11.66	303	603	6.91	8.65	22	3.71	32	666	857	809
Calcium hypochlorite (briquettes)	Carton1	12.02	403	839	16.54	19.92	36	4.38	38	793	651	1,081
Calcium hypochlorite (granular)	Carton1	11.40	414	800	14.66	18.81	26	5.06	37	829	300	1,002
48-lbs (21.8 kg) Net Weight Packaged Material												
Sodium chloride (tablets)	2 Pails	20.33	30	37	0.15	0.35	nd	nd	7	154	174	572
Trichlor (tablets)	2 Pails	24.50	21	49	1.25	1.23	440	0.34	16	461	235	279
Sodium percarbonate (65%)	2 Pails	23.61	76	149	4.6	4.66	96	0.5	13	572	458	742

Test Pkg: Carton 1= 6 HDPE containers in DW carton; Carton 2= 24 1-lb bags in DW carton; Pail = 2.5 gallon HDPE pail with lid; nd = not distinguishable from burner baseline; nr = not recorded

Correlations

Visual observations of the packaged oxidizer when exposed to an external fire correlated very well with the recorded test data. Once ignited, oxidizers that produced vigorous burning had high peak heat release rates and high radiant heat flux, short burning times, and generally higher mass loss rates. Oxidizers that did not produce vigorous burning had low to intermediate peak heat release rates and radiant heat flux, longer burning times, and generally lower mass loss rates. Oxidizers observed to generate significant gaseous products when exposed to the burner and/or during combustion similarly showed high smoke production rates.

Data collected from the different types of oxidizers in the same quantity and test packaging were correlated using scatter plots. Figure 15 shows the positive linear correlation between the peak convective heat release rate and the peak radiant heat flux. The peak incident radiant heat flux at the lower target at a fixed distance from the packaged test material was consistently 5–8% of the peak convective heat release rate.
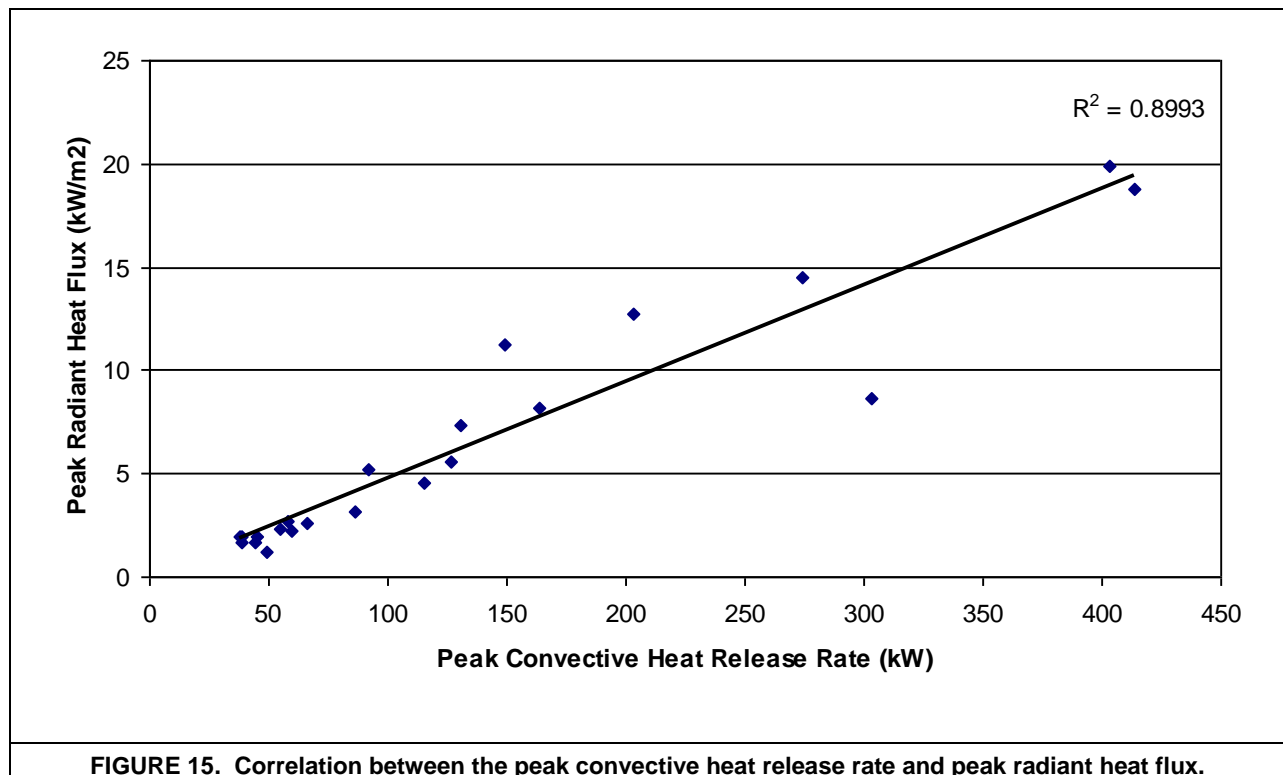
FIGURE 15. Correlation between the peak convective heat release rate and peak radiant heat flux.

The duration of active burning was calculated from the radiant heat flux profiles, as illustrated in Figure 16. The 'active burning time' based on the heat flux peak width at half height was chosen to facilitate reproducible data reduction rather than as a realistic description of the entire time involved in a burn. The mass loss rate was calculated over the duration of active burning. Linear regression of mass loss over the duration of active burning had r-square values greater than 0.95. The active burning time decreased (Figure 17) and the mass loss rate generally increased (Figure 18) with increasing peak heat release rate.

Peak radiant heat flux= 15.6 kW/m²
1/2 Peak =7.8 kW/m²
Active burning time=width at 1/2 peak=56s
MLR=4.6 kg/min (R²=0.99)
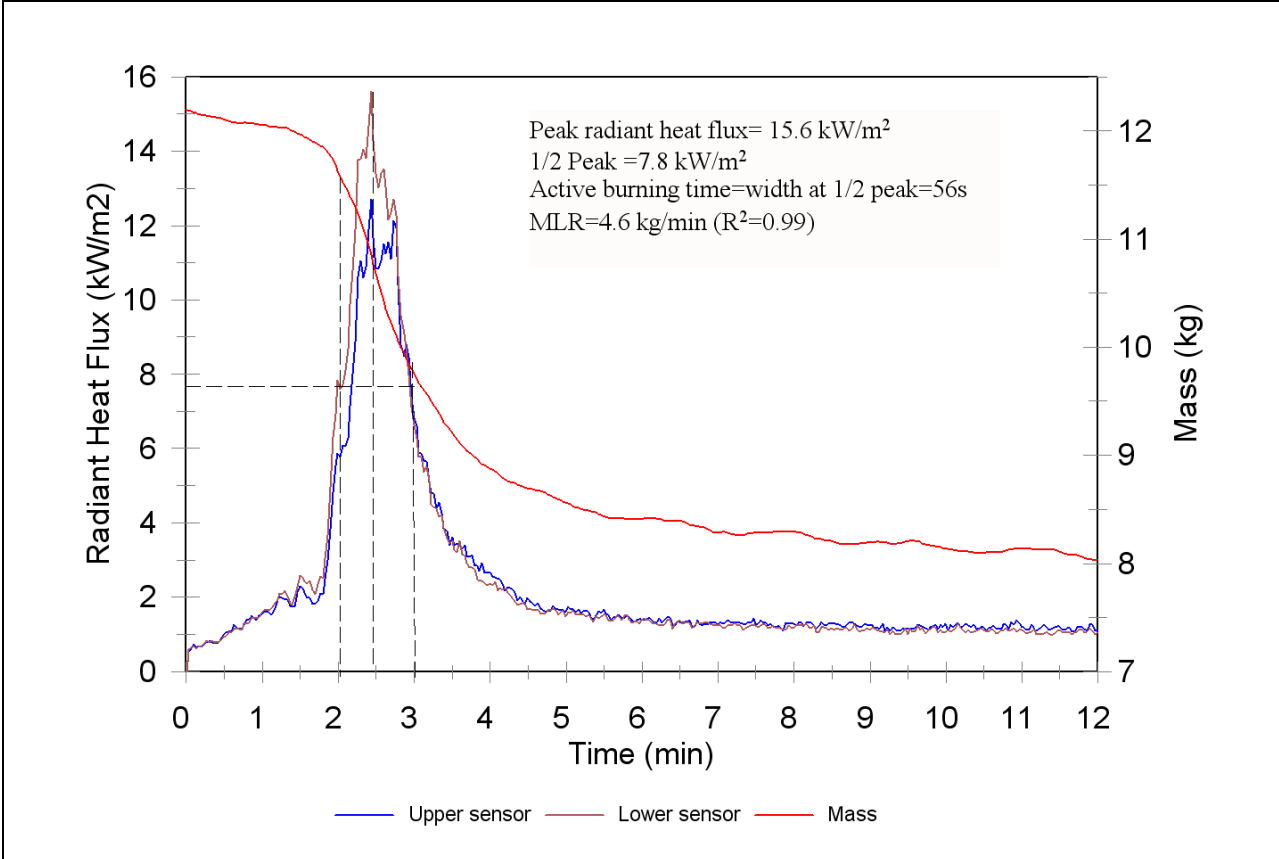
FIGURE 16. Radiant heat flux and mass loss profile of packaged oxidizer illustrating the active burning time and mass loss rate calculated from the width at one-half the peak radiant heat flux.

$R^2 = 0.8689$
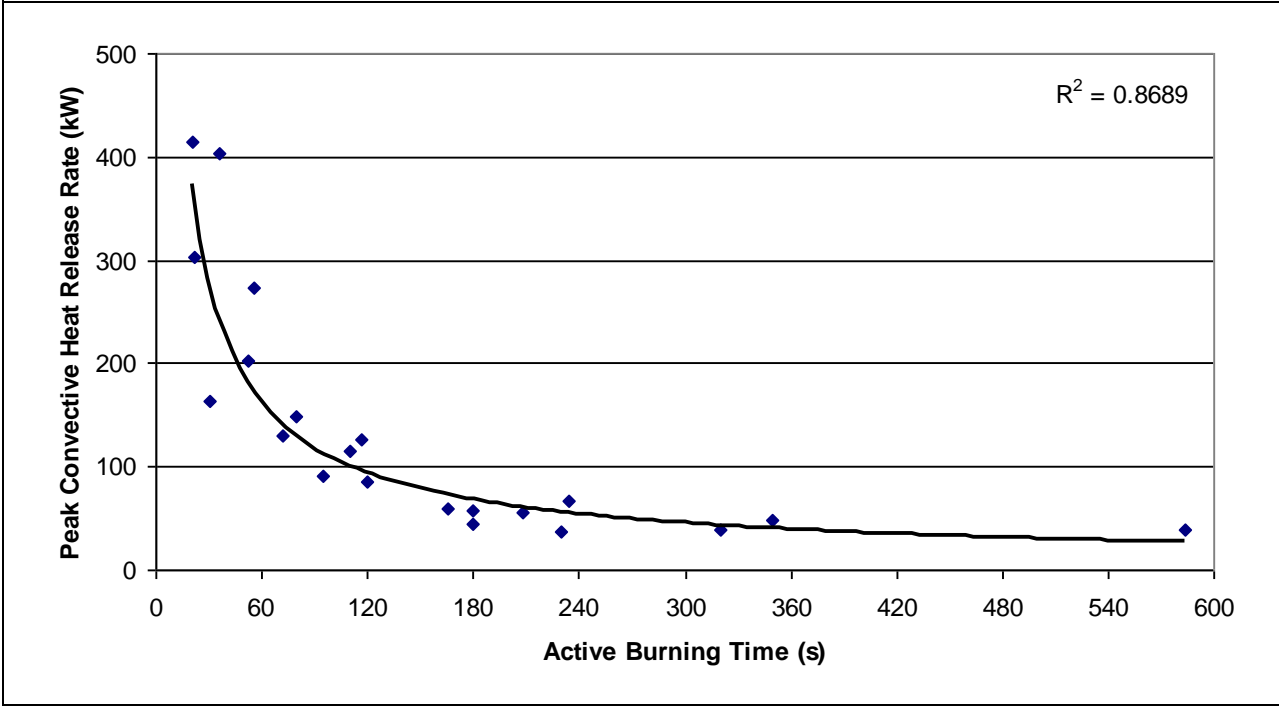
FIGURE 17. Correlation between the active burning time and peak convective heat release rate data from the intermediate scale tests with 24-lbs net weight packaged salt and oxidizers in the test packaging.

FIGURE 18. Correlation between the mass loss rate and peak convective heat release rate data from the intermediate scale tests with 24-lbs net weight packaged sodium chloride and oxidizers in the same combustible test packaging.
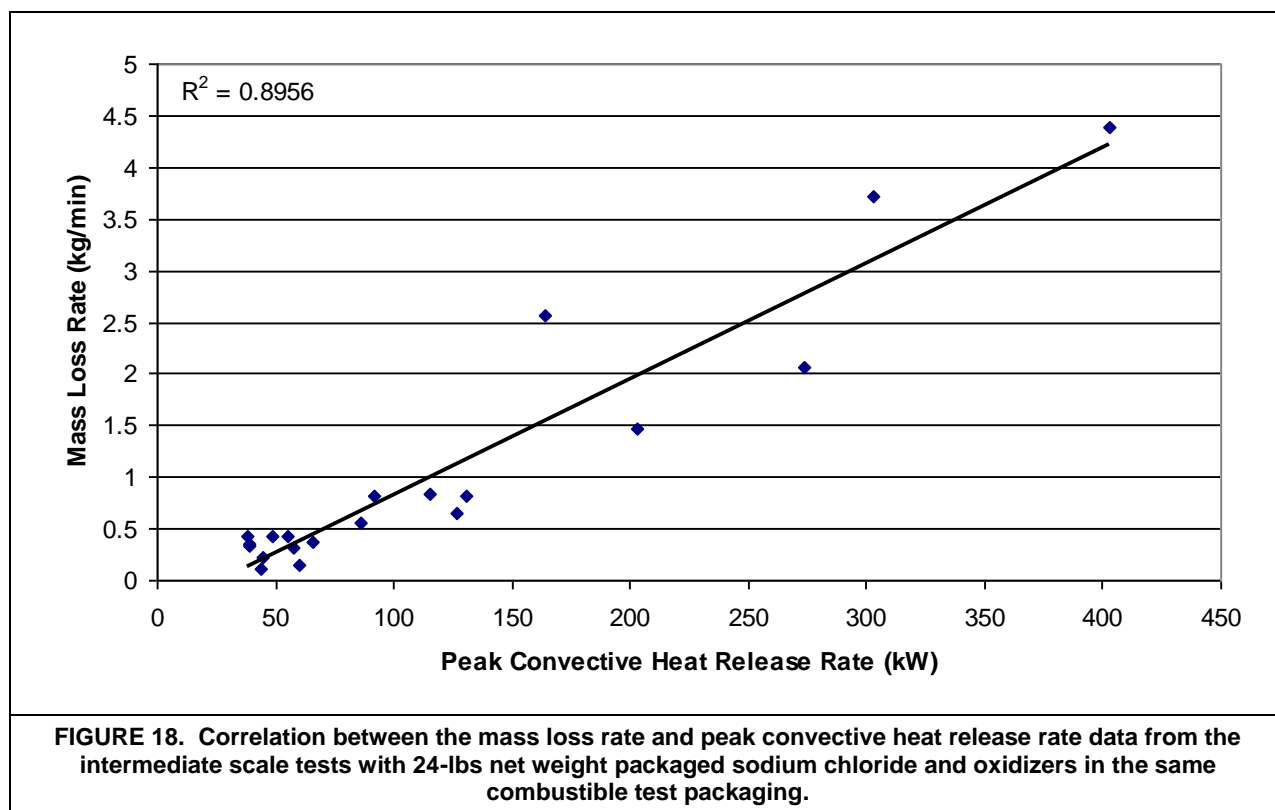
The peak heat release rates, based on carbon dioxide generation and on gas temperature rise, showed a strong correlation (Fig. 19). Under test conditions, the ratio of the peak convective to peak chemical heat release rate (peak HRR_{conv}/ peak HRR_{CO2}) was 51±10% (Fig. 20)—meaning the heat release rate ratio did not depend on the chemical composition. In Figure 20, the apparent outlier for 1:1 calcium hypochlorite:sodium chloride in 1-lb bags is likely the result of the hood blower (volumetric flow) increasing just as the packaged test material ignited and fire rapidly spread causing a dilution in the heat resulting in a lower temperature and a lower peak convective heat release rate.

Figure 21 shows the peak convective heat release rate and peak heat release rate based on carbon dioxide generation for the packaged sodium chlorite and various oxidizers in the same test packaging in order of increasing peak convective heat release rate. The range in peak heat release rate was consistent with the anticipated and observed range in burning behavior. As expected, the peak convective heat release rate was lower than the chemical heat release rate. About two-thirds of energy generated by a fire is released through convection.[17] The ratio of the total convective heat released (THR_{conv}) for the packaged oxidizers to the total chemical heat released (THR_{CO2}) was 68±19%.
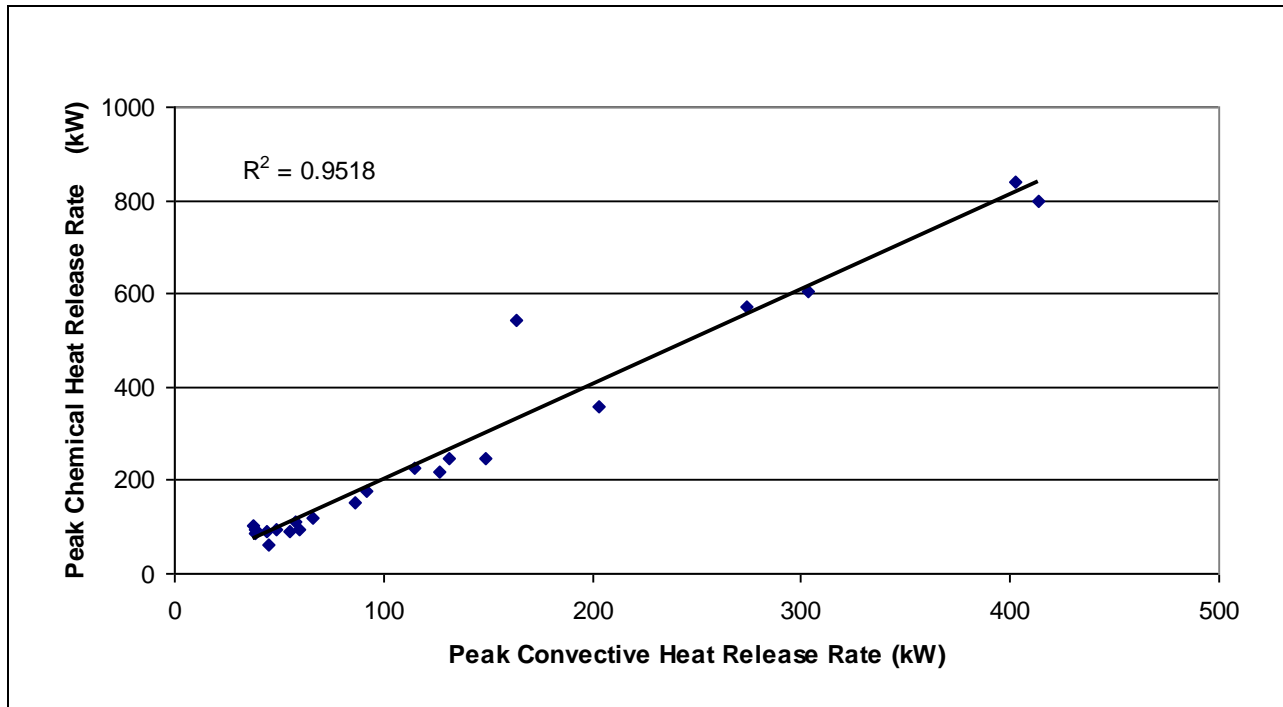
FIGURE 19. Correlation between the peak heat release rate based on carbon dioxide generation and gas temperature rise from tests with 24-lbs net weight packaged sodium chloride and oxidizers.
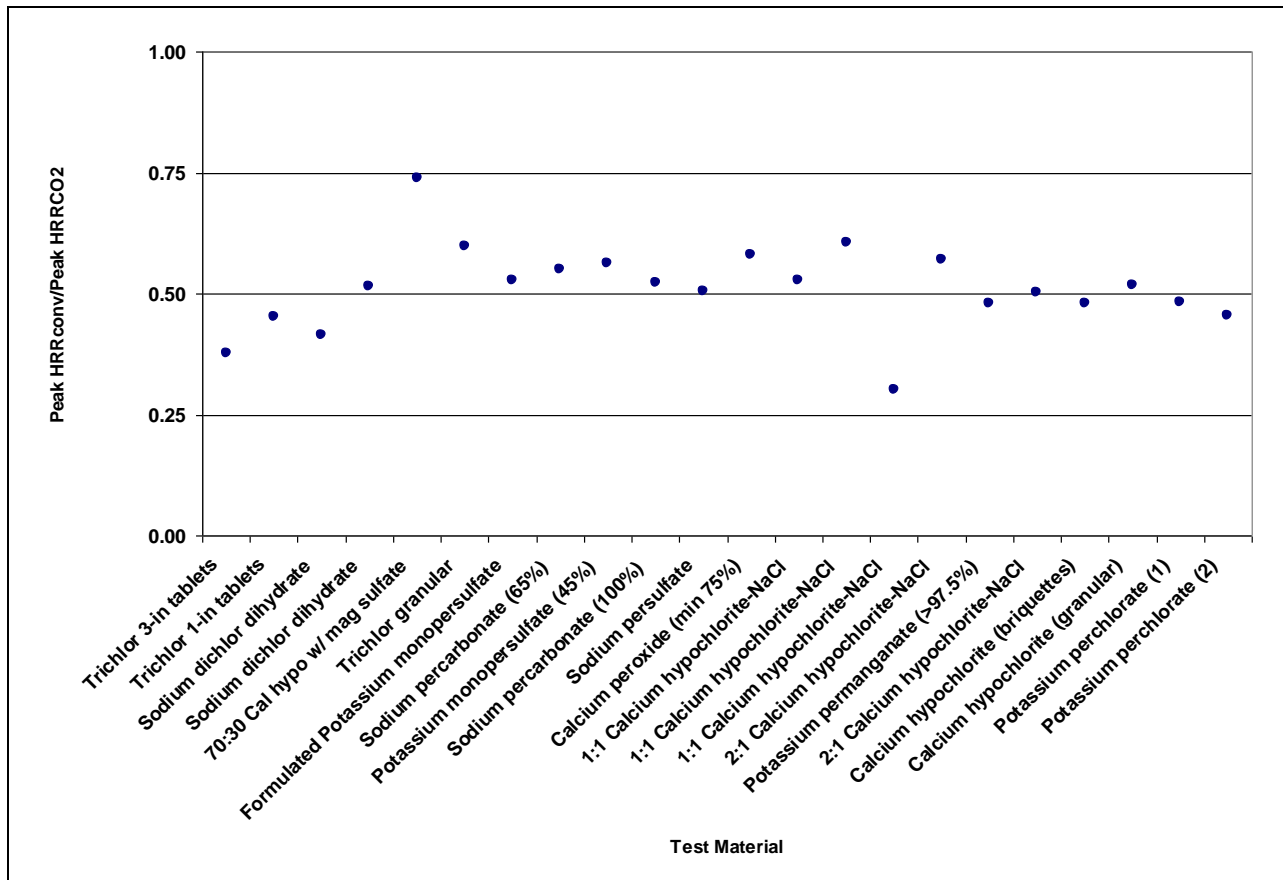
FIGURE 20. Ratio of the peak convective to peak chemical heat release rate of the oxidizers tested including potassium perchlorate.
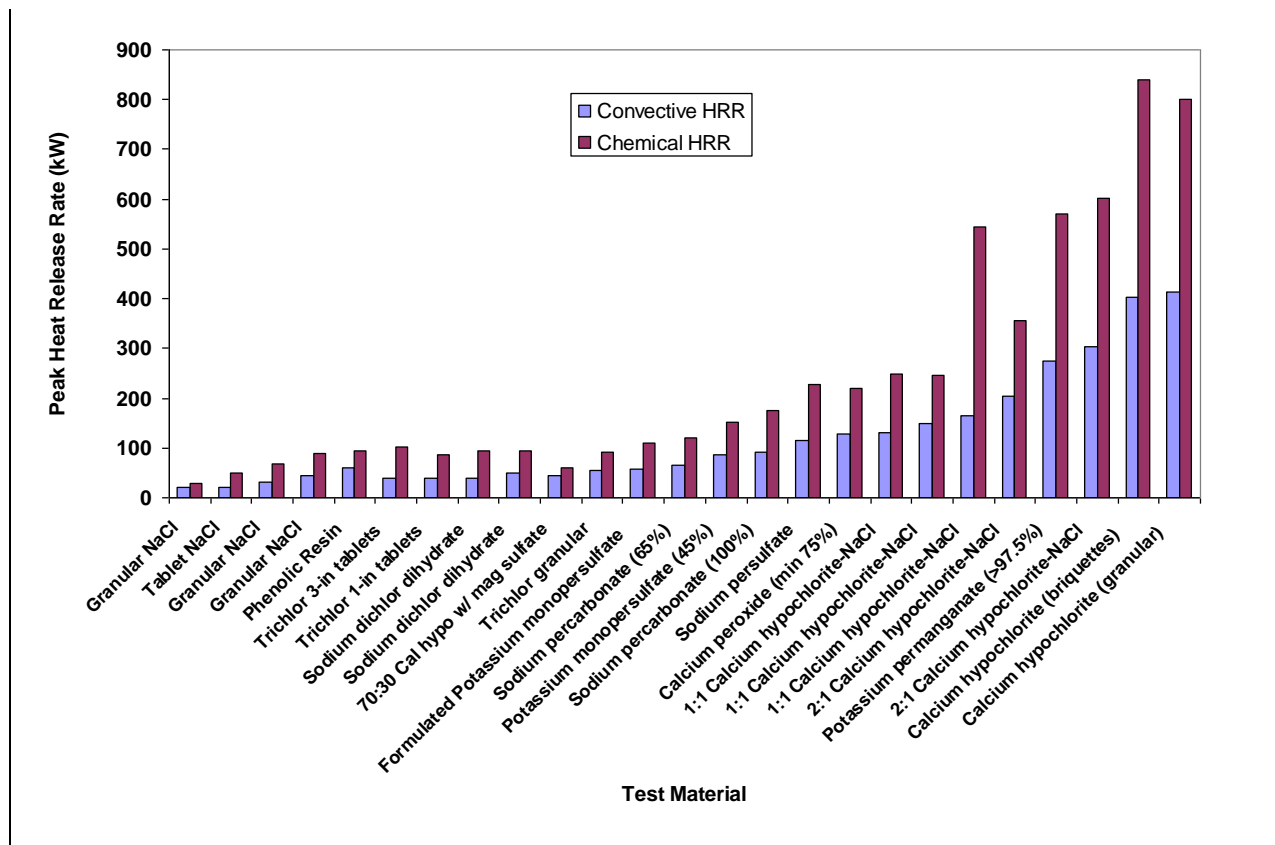
FIGURE 21. Peak heat release rates of 24-lb of sodium chloride, phenolic resin powder and oxidizers based on carbon dioxide generation and gas temperature rise.

For the range in oxidizer burning behavior, the heat release rate, radiant heat flux, and surface temperature profiles were consistent; in other words, the general shape of the data profiles were the same. The radiant heat flux transducers were the closest non-contact sensors to the fires and provided the best characterization of fire growth and intensity when comparing oxidizers. The steady increase in the radiant heat flux correlated with the visual increase in burning behavior. The peak visual burning behavior corresponded to the time of peak radiant heat flux. A decrease in visual burning behavior correlated with a steady decrease in the radiant heat flux toward baseline burner values.

Inert Material, Organic Resin, and Oxidizer Test Results

A majority (25/32) of the intermediate-scale tests consisted of 24 pounds of test material (i.e., common salt or oxidizer) in combustible test packaging. The approximate weight percent sodium chloride and oxidizer in the HDPE containers in DW cartons was 89%; 93 wt% when packaged in 1-lb bags in a DW carton; and 94 wt% when packaged in a 2.5-gallon HDPE pail.

Figures 22 and 23 show the peak convective heat release rate, peak radiant heat flux and active burning time of empty test packaging, packaged sodium chloride, phenolic resin powder, and various oxidizers, respectively. The figures clearly illustrate the range in burning behavior of the different types of oxidizers.
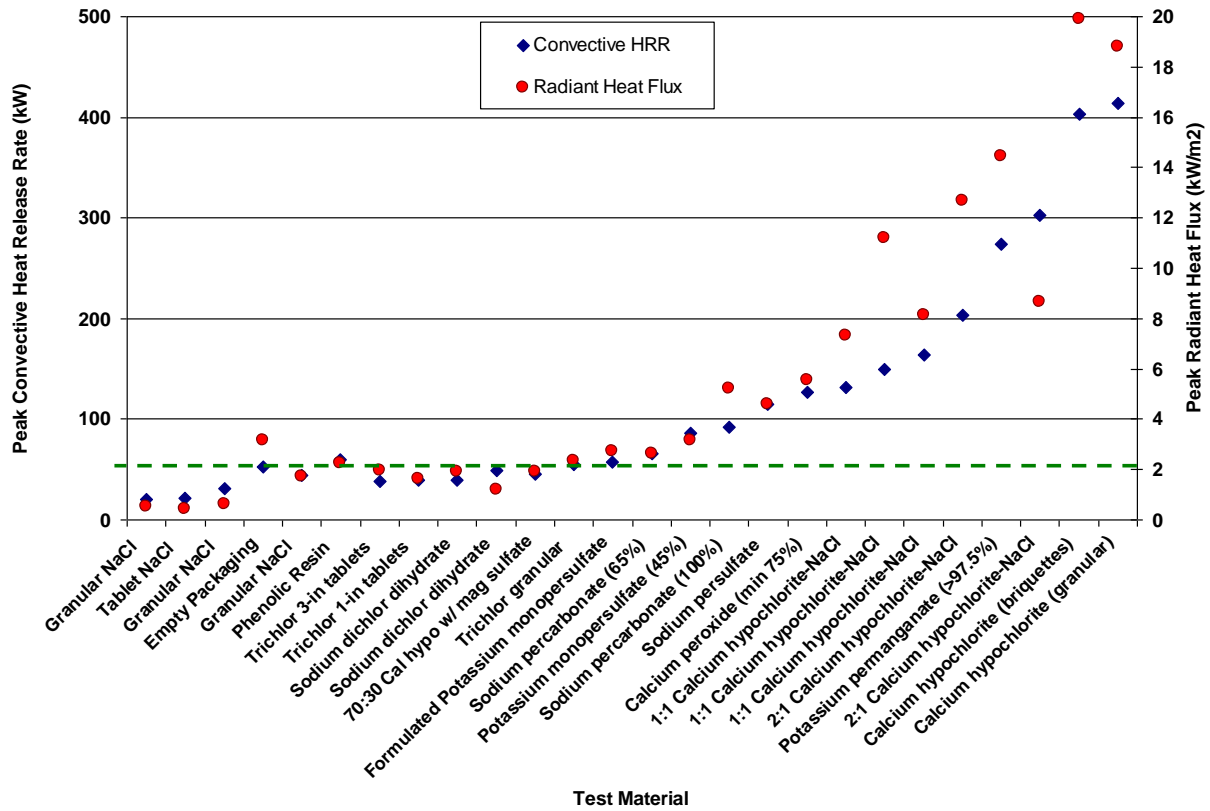
FIGURE 22. Peak convective heat release rate and peak radiant heat flux from empty test packaging and 24-lbs packaged sodium chloride, phenolic resin powder and oxidizers.
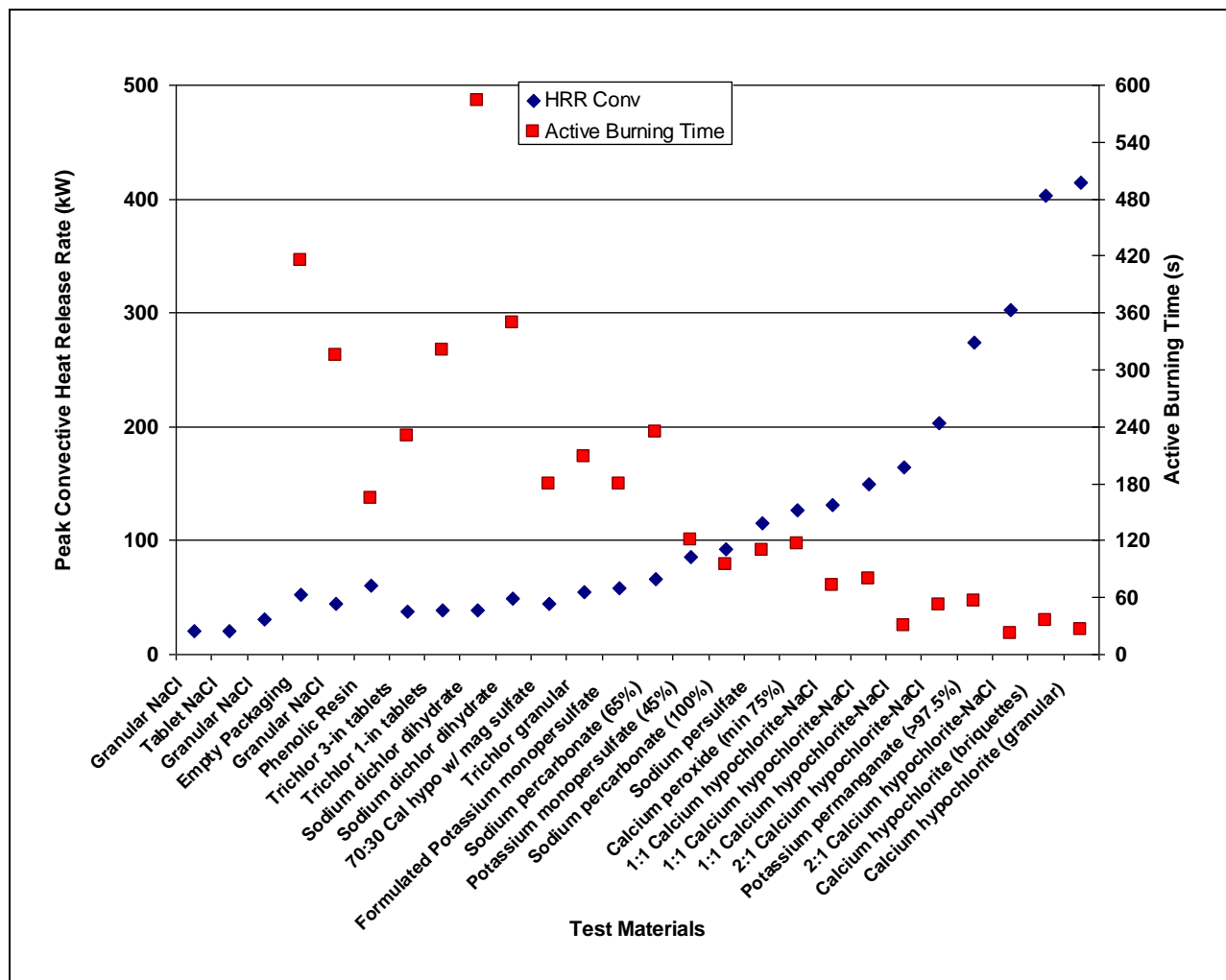
FIGURE 23. Peak convective heat release rate and active burning times of empty test packaging, 24-lbs packaged sodium chloride, phenolic resin powder and oxidizers. Note, the active burning time data for some tests were greater than 600 seconds or not distinguishable from the burner baseline.

The empty combustible test packaging was completely consumed. Its peak convective heat release rate was 53 kW (less the burner) at 6 minutes 38 seconds after the burner was ignited. The peak radiant heat flux from the empty packaging was 3.15 kW/m^2. The dashed line in Figure 22 is drawn through the peak convective heat release rate of the empty packaging for ease in comparison with packaged sodium chloride, the phenolic resin and oxidizers.

When the test packaging contained granular or tablet salt, the peak convective heat release rate and radiant heat flux were reduced. The crystalline or tablet form sodium chloride did not cause an increase in the burning rate of the combustible test packaging. The peak convective heat release rates of sodium chloride in the combustible packaging ranged from 20–44 kW; the peak radiant heat flux ranged from 0.4–1.7 kW/m^2. The duration of active burning could not be calculated because the heat flux profile from the packaged salt was hardly distinguishable from the burner baseline. At the end of the tests involving sodium chloride, there was unconsumed and protected corrugated board carton which was consistent with the low peak temperatures measured at the bottom of the carton.

The peak convective heat release rate of the test packaging with phenolic resin powder was 60 kW (convective) and 94 kW (chemical) compared to 73 kW (chemical) for the empty packaging. The peak radiant heat flux of the resin (2.25 kW/m^2) was lower than the empty packaging (3.09 kW/m^2) but higher than the packaged common salt (0.65 kW/m^2). Twenty-eight weight percent of the packaged resin decomposed and/or burned. While the phenolic resin did contribute to the heat release rate, the difference was not considered a "moderate increase" in the burning rate of the combustible packaging. The duration of active burning and the mass loss rate of the packaged phenolic resin were 165 seconds and 0.15 kg/min, respectively.

The peak convective heat release rate of the oxidizers (24-lbs net weight) in the test packaging ranged from 38–414 kW. The peak heat release rate based on carbon dioxide generation ranged from 61–839 kW. The peak incident radiant heat flux ranged from 1–20 kW/m^2: the lowest was sodium dichlor in a HDPE pail and the highest heat came from the fire involving high strength calcium hypochlorite briquettes in HDPE containers. The mass loss rate ranged from 0.2 kg/min for calcium hypochlorite formulated with magnesium sulfate heptahydrate to 5.1 kg/min for non-formulated or high-strength calcium hypochlorite. The burning duration calculated from the radiant heat flux profiles ranged from 22 seconds (2:1 cal hypo:salt) to over 9 minutes (dichlor in a pail).

Referring to Figure 22, four materials had peak convective heat release rates and peak radiant heat flux lower than the empty combustible test packaging and phenolic resin but higher than packaged common salt. These materials were granular and tablet form trichlor, granular and tablet form dichlor, granular 70:30 calcium hypochlorite with magnesium sulfate heptahydrate and a formulated granular commercial product containing less than 45% potassium monopersulfate (or less than 90% triple salt). The active burning times were 3 minutes or longer. These materials did not cause a visual increase in the burning rate of the combustible test packaging. Then, starting with sodium percarbonate (65%), the test data in Table 8 and in Figure 22 show a gradual increase in the peak convective heat release rate and peak radiant heat flux compared to the combustible test packaging.

While lower than the empty packaging, the formulated potassium monopersulfate product and formulated sodium percarbonate (65%) had peak radiant heat flux ~78% higher than sodium chloride in identical packaging. A gradual but notable increase in visual burning intensity was observed and indicated by even higher radiant heat flux from the fires involving neat potassium monopersulfate (45% or 90% triple salt) and sodium percarbonate (99%). The measured surface temperature of test materials with peak convective heat release rate less than 100 kW, or approximately twice the peak convective heat release rate of the test packaging, ranged from 420–722°C. Temperatures inside the packaging ranged from 362–940°C. With the exception of sodium percarbonate (99%), the calculated durations of active burning were greater than 2 minutes.

Seven oxidizers had peak convective heat release rates greater than 100 kW or more than double the peak convective heat release rate of empty test packaging. Three test materials had peak convective heat release rates between 100–200 kW. These were 99% sodium persulfate (115 kW), 75% calcium peroxide (127 kW) and 1:1 calcium hypochlorite-sodium chloride (33% available chlorine) in three different packaging (131-164 kW). The peak radiant heat flux from these materials ranged from 3.5–11.2 kW/m^2. The measured surface temperature ranged from 630–793°C. The temperatures inside the carton ranged from 659–1,012°C. With the exception of 1:1 calcium hypochlorite: sodium chloride in 1-lb bags, the calculated active burning times of these materials were less than or equal to 2 minutes.

Four oxidizers showed vigorous burning behavior with peak convective heat release rates greater than 200 kW and as high as 414 kW. These materials were potassium permanganate (274 kW), 2:1 calcium hypochlorite-sodium chloride (48% available chlorine) in HDPE containers (203 kW) and 1-lb bags (303 kW), high-strength granular (414 kW) - and briquette (403 kW)- calcium hypochlorite, and potassium perchlorate (152 – 195 kW). The tests involving these materials were generally shorter in duration, hotter, and had higher or faster mass loss rates. The peak radiant heat flux from the packaged oxidizers ranged from 8.6–20 kW/m^2, surface temperatures ranged from 666–1,168°C, and material temperatures ranged from 733–1,317°C. The duration of active burning was less than 60 seconds. The mass loss rates ranged from 1.5–5.1 kg/min (3.3–11.1 lbs/min). Only 12 lbs of potassium perchlorate in combustible test packaging were exposed to the propane burner. This material was shipped and received in a plastic bag inside a metal pail and transferred to the combustible test packaging. The decision to first test 12-lbs of material was based on the burning behavior, mass loss rates, and active burning time data from the bench-scale screening tests and the FPA test data. Once the packaging was compromised, the material burned vigorously. Welding safety glasses were required to view the flames at the area of the package on the table. Twelve pounds of potassium perchlorate resulted in peak convective heat release rates ranging from 152–195 kW, peak radiant heat flux up to 12.5-kW/m^2, and active burning times ranging from 26–50 seconds.

The maximum surface temperatures recorded during each fire exposure test are listed in Table 8. Table 9 summarizes the duration of time at temperatures greater than 700°C (1,292°F).

TABLE 9. Test Materials with Sustained Surface Temperatures Greater than 700°C

Oxidizer (Packaging)	Duration of Surface Temperature Greater than 700°C (s)
1:1 Calcium hypochlorite-sodium chloride(HDPE containers)	5
1:1 Calcium hypochlorite-sodium chloride (HDPE pail)	15
1:1 Calcium hypochlorite-sodium chloride (1-lb bags)	29
Sodium percarbonate (99%) (HDPE containers)	11
Granular high-strength calcium hypochlorite (HDPE containers)	20
Briquette high-strength calcium hypochlorite (HDPE containers)	37
Potassium perchlorate (three 12-lb trials) (HDPE containers)	13, 27, 31
Potassium permanganate (HDPE containers)	46
2:1 Calcium hypochlorite-sodium chloride (HDPE containers)	61
Calcium peroxide (HDPE containers)	102

To demonstrate the range in burning behavior and the acceleration of burning rate by oxidizers exposed to an external fire, the radiant heat flux profiles of four, similarly-packaged test materials are compared in Figure 24. The range in burning rate is demonstrated by the range in the peak heat flux, the width of the peaks, the time to the peak, and rate in growth of the fire (i.e., rate of rise in radiant heat flux).
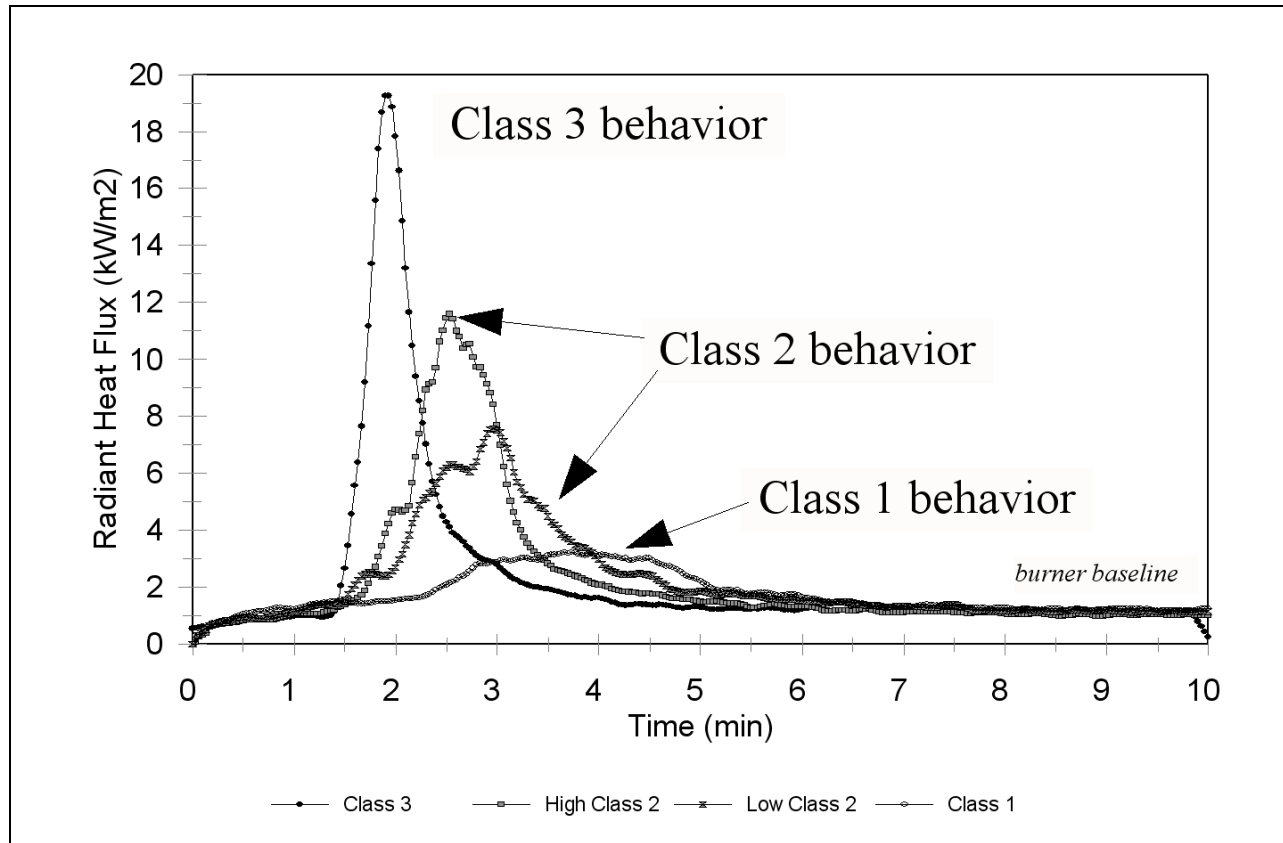
FIGURE 24. Radiant heat flux profiles of oxidizers with a range in burning behavior.

Packaging did show an influence on burning behavior of oxidizers that exhibited Class 2 behavior. Figure 25 shows the radiant heat flux profiles of 1:1 calcium hypochlorite-sodium chloride in 6 HDPE containers in a doubled-wall carton, twenty-four 1-lb bags in a doubled-wall carton, and a 2.5-gallon HDPE pail. The peak convective heat release rate of the same material in the three different types of combustible test packaging ranged from 131–164 kW. Once the carton was compromised, the ignition and spread of fire through the mixed-orientation 1-lb bag was rapid. The duration of active burning was 30 seconds; the peak convective heat release rate occurred 19 seconds after the first visual involvement of the oxidizer. The 2.5-gallon pail required more time to penetrate but, once compromised, resulted in rapid fire growth. The duration of active burning was 80 seconds, and the peak convective heat release rate occurred at 43 seconds after the first visual involvement of the oxidizer. When packaged in 6 HDPE containers, the peak convective heat release rate was 131 kW, the duration of active burning was 72 seconds and the time from first visual involvement of the oxidizer to the peak convective heat release rate was 76 seconds. The mass loss rate of the oxidizer packaged in 1-lb bag was 2.56 kg/min compared to 0.81 kg/min in HDPE containers. Twenty-one weight percent each of the oxidizer packaged in 1-lb bags and in 60-ounce containers were consumed[**].

A similar influence of packaging on the peak convective heat release rate and active burning time was observed with the 2:1 calcium hypochlorite-sodium chloride admixture in 1-lb bags and in HDPE containers (Fig. 26). The peak convective heat release rates for the material in HDPE

[**] Mass loss was not recorded for the calcium hypochlorite-sodium chloride admixture in the pail.

containers and in 1-lb bags were 203 kW and 303 kW, respectively. The time to the peak convective heat release rate after the time of first visual involvement of the oxidizer was 8 seconds for the material in twenty-four 1-lb bags compared to 43 seconds in six 4-lb capacity HDPE containers. The calculated duration of active burning was 22 seconds for the 1-lb bags and 52 seconds for the HDPE containers. In other words, the packaging resulted in a 100-kW difference and a significant decrease in the time of first visual involvement of the oxidizer. The fire involving the 2:1 calcium hypochlorite-sodium chloride in 1-lb bags was so rapid that it caused an inversion in the oxygen concentration data profile, indicating that oxygen was generated *and* at a greater rate than the oxygen consumed during vigorous combustion (Fig. 27). For this reason, the heat release rate based on oxygen consumption principles is not valid for oxidizers that release oxygen as an oxidant.
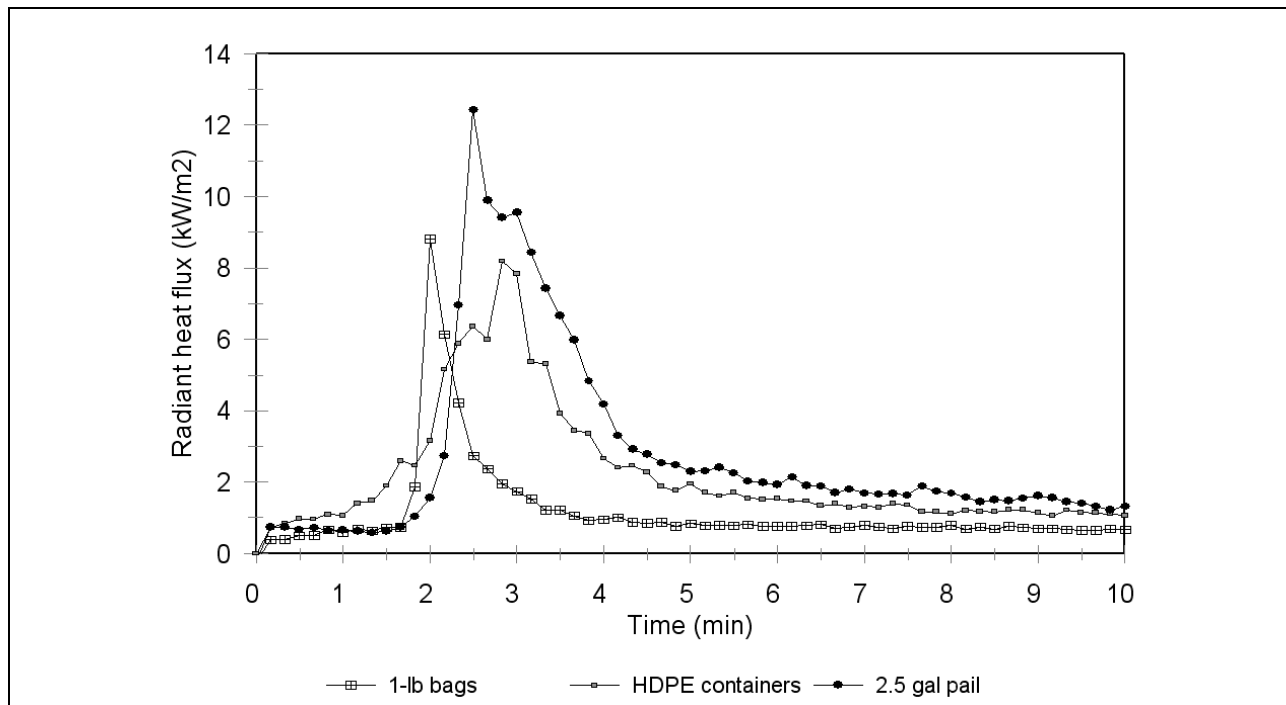
FIGURE 25. Radiant heat flux profiles of 24 lbs net weight 1:1 calcium hypochlorite-sodium chloride in three different packaging.
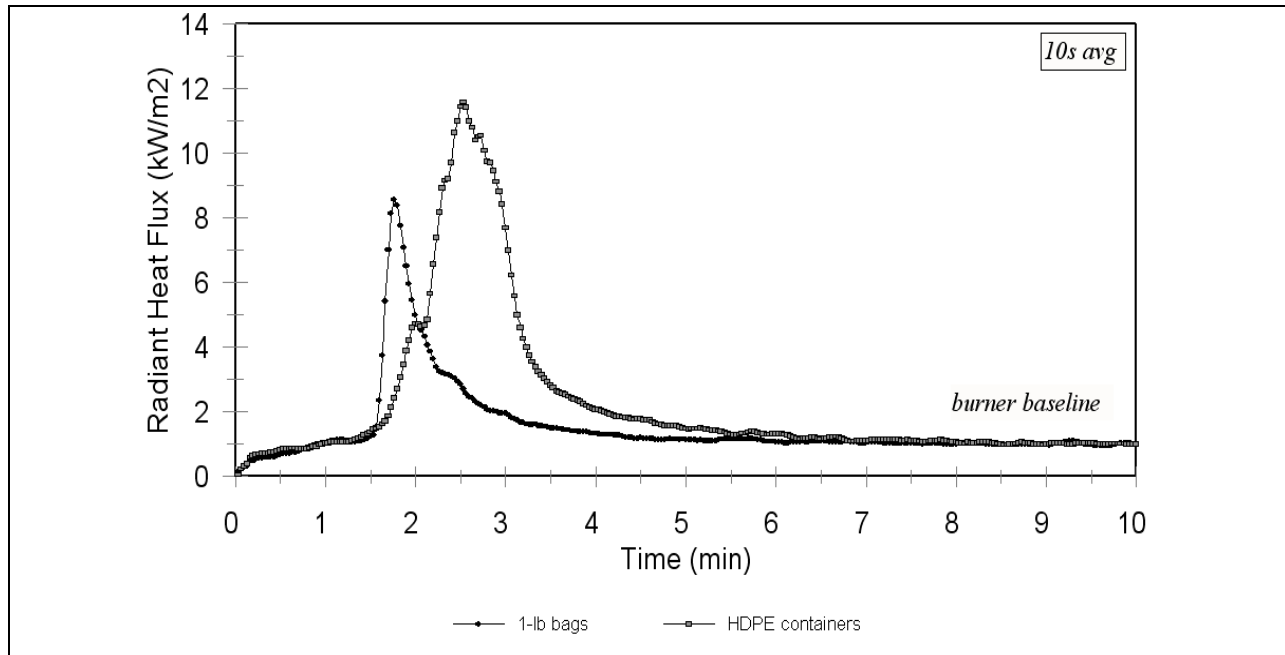
FIGURE 26. Radiant heat flux profiles of 24 lbs net weight 2:1 calcium hypochlorite-sodium chloride in HDPE containers and 1-lb bags.
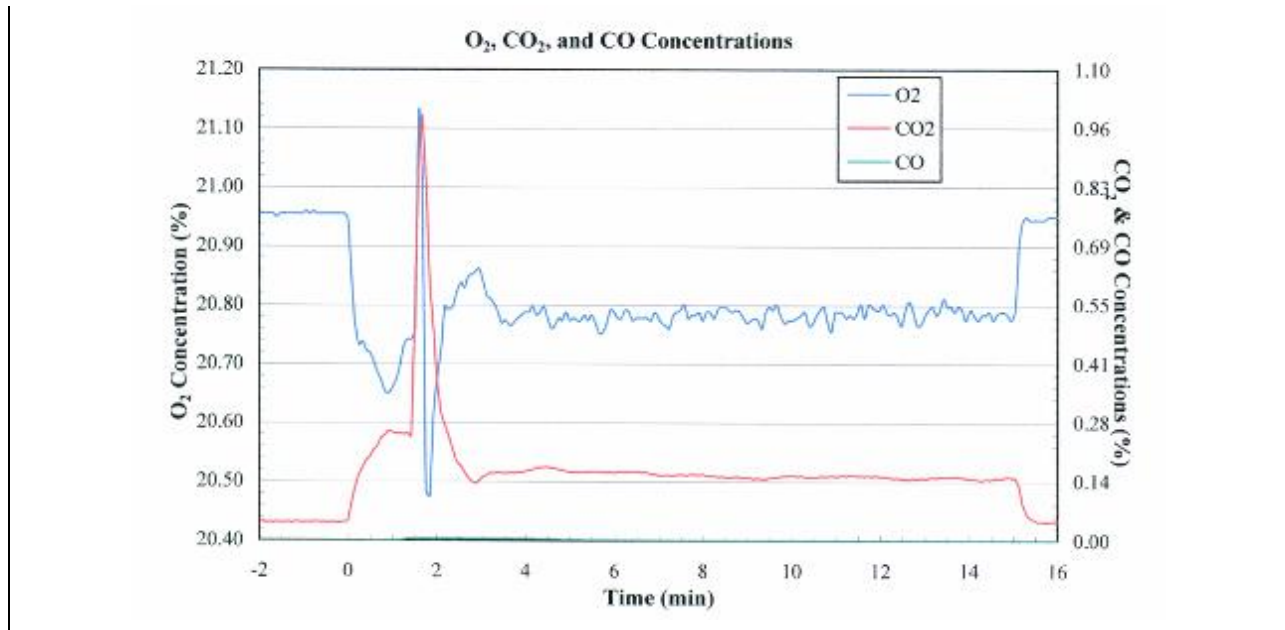
FIGURE 27. Inversion in the oxygen concentration of the combustion gas during the fire exposure test with 2:1 calcium hypochlorite-sodium chloride in twenty-four, 1-lb bags.

The intermediate-scale fire exposure test and peak heat release rate distinguished between pure and formulated oxidizers and oxidizers admixed with a hydrated salt. In the same combustible test packaging, the peak convective heat release rate of high-strength calcium hypochlorite (72.6% available chlorine, 5.6% water) was reduced 51% when diluted in the 2:1 sodium chloride admixture and 68% in the 1:1 sodium chloride admixture. When admixed with the hydrated salt, the peak convective heat release rate of high-strength calcium hypochlorite was reduced 89%. Similarly, the peak convective heat release rate of sodium percarbonate

(99%) was reduced 26% when formulated to 65% with the non-oxidizer sodium carbonate (i.e., soda ash). The peak heat release rate of neat potassium monopersulfate (45%) was similarly reduced from 86 kW to 58 kW when formulated, representing a 33% reduction in the peak heat release rate.

Product form (granular vs. tablet) had a lesser influence on burning rate than composition and formulation. Three materials were tested using granular and tablet product forms: sodium chloride, trichloroisocyanuric acid and high-strength calcium hypochlorite. In all three cases, the peak heat release rate from the tablet-form material was lower than the granular-form. The peak convective heat release rate of trichlor was reduced by 29% for both 1-inch and 3-inch diameter tablets (i.e., independent of tablet size). The mass of material consumed during the tests with the granular and 1-inch diameter tablet trichlor was the same (~35 wt%); the mass loss rate of the 1-inch tablets (0.36-kg/min) was slightly lower than the granular trichlor (0.42-kg/min). The peak convective heat release rate of briquette form high-strength calcium hypochlorite compared to the granular form was only reduced by 3%. The mass consumed during the two tests with high-strength calcium hypochlorite were the same (~38 wt%); the mass loss rate of the briquettes (4.4 kg/min) was slower than the granular material (5.1 kg/min). In both cases, the tablet form did not change the burning behavior expected of the Class of oxidizer.

Two materials with Class 1 behavior, tablet-form trichlor and sodium percarbonate (65%), were tested at 24 lbs in HDPE containers in cartons and also at 48-lbs in two 2.5-gallon HDPE pails. The peak convective heat release rate did not increase significantly with the additional Class 1 oxidizer, so the packaging was less influential on the fire hazard. For the Class 1 materials tested at 48 lbs, the peak convective heat release rate remained less than 100 kW. Doubling the mass (i.e., from 24 lbs to 48 lbs) of Class 2 and Class 3 materials is expected to result in higher heat release rates.

The 2-MW hood and 24-lb scale effectively captured the range in enhancement or acceleration of burning rate by oxidizers. The 4 m^3/s volume flow rate of the exhaust collection duct was sufficient to capture the range in volume of gaseous products generated. Some oxidizers released significant gaseous products, due to decomposition or rapid combustion. The 12–24-lb scale was sufficient to quantify the heat release rate without the loss of gaseous products from the hood. Twenty-four pounds of high-strength calcium hypochlorite (72.6% available chlorine, 5.6% water) had a peak chemical heat release of ~820 kW (Fig. 28), and significant gaseous products were generated; 48 lbs would have overcome the 2-MW hood and/or a volume flow rate less than 4 m^3/s. Twelve pounds (12 lbs) of potassium perchlorate burned vigorously with significant gaseous products generated (Fig. 29); 24 lbs of potassium perchlorate would have overcome the hood and/or a volume flow rate less than 4 m^3/s.
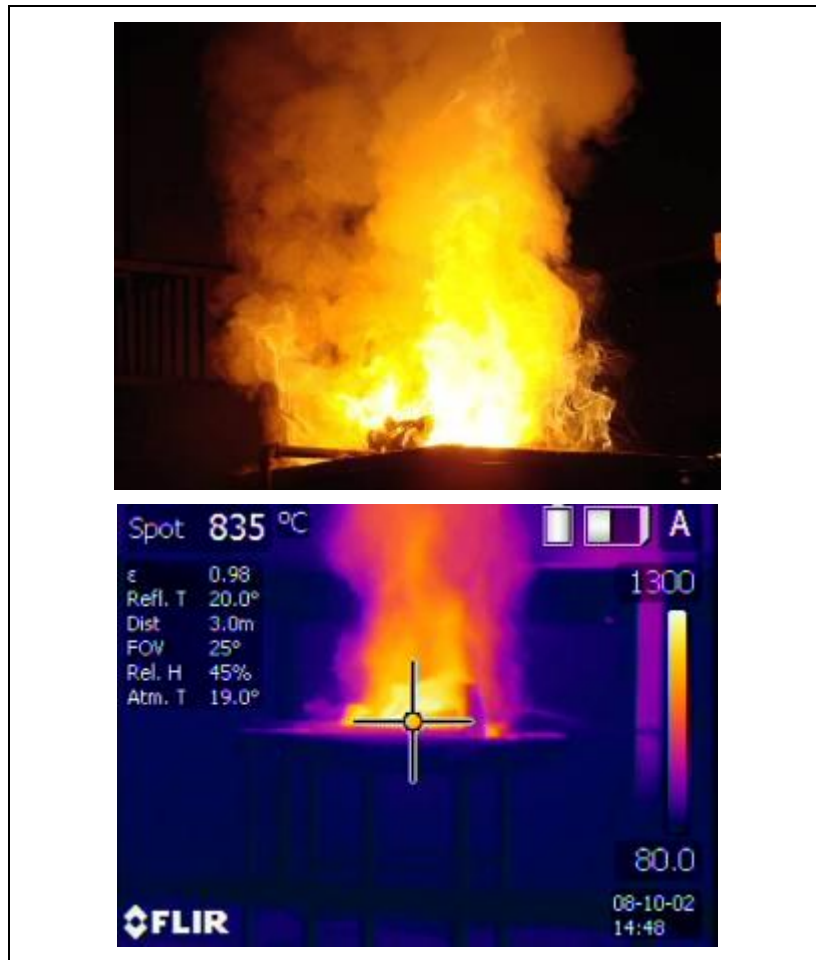
FIGURE 28. Photograph and thermal image during test with high strength calcium hypochlorite.

FIGURE 29. Fire exposure test with 12-lbs potassium perchlorate.

Bench-Scale Screening Test Results

In the absence of direct or indirect calorimetric measurements, the burning rate of oxidizer-cellulose powder mixtures can be described by the mass loss rate, burning time, flame temperature and approximate peak flame height. For oxidizer cellulose powder mixtures that ignited and burned with flaming combustion, mass loss rate and active burning time are sufficient to characterize and compare burning rate.   Thermocouples above the pile really distinguish between decomposition without flaming combustion (e.g., low temps) and combustion (e.g., high temperatures). The active burning time provides information on the rate at which the mixture is decomposing or burning.   Mass loss is a recognized fire-test-response characteristic used in ASTM fire test methods. In ASTM E 2102, for example, mass loss and ignitability are used for screening purposes, specifically "to determine whether a material, product or assembly: (a) exhibits any unusual fire-related characteristics; (b) has certain expected fire-related characteristics; or (c) is capable of being preliminarily categorized according to the fire characteristic in question".[18]   The burning rate of the various oxidizer-cellulose powder mixtures were compared with the sodium chloride-cellulose powder mixtures.

The acquisition of mass loss and temperature data was terminated at the end of visible flaming combustion.   The final measured mass (m_f) was used to calculate the mass of the mixture during combustion at 20%, 50%, and 80% consumed. The final measured mass was also used to calculate the total mass lost (i.e., percent consumed). Linear regression of independent- time and dependent-mass data from 20–80% of the final measured mass resulted in the mass loss rate and typically had r-squared values greater than .96 and more often .99. The active burning time was calculated from the time of first measurable steady mass loss to the time at 80% mass lost. The time to 50% consumed, the time from first recordable mass loss to the time at 50% mass loss, was also evaluated as a potential indicator of burning duration.

The advantages of the bench-scale screening test to assess the burning rate of different, granular oxidizers are: 1) mass loss is a fire-test-response characteristic, 2) it can be performed by lab technicians using typical laboratory equipment and low expense, 3) can be used to examine both oxidizer pure materials, admixtures, different particle size and different fuels, and, 4) provides more information including test-operator-independent burning time durations.   In addition to mass loss data, thermocouples in the plume directly above the pile provided even more data including plume temperatures and approximate peak flame height to characterize burning rate.   Evaluation of the materials chemical structure before testing and the review of other additional decomposition data should be done before testing. The bench-scale screening test cannot incorporate all factors required for fire hazard or fire risk assessment of oxidizers, specifically thermal instability, decomposition, and reactivity or behavior under actual fire conditions.

Cellulose Powder

Thirty grams of cellulose powder filled the 100-mL funnel. It was easily ignited by the glowing wire and spread flaming combustion over the pile. When the entire pile was involved, the peak flame height reached 9 inches above the test platform. The cellulose powder continued to burn after the wire opened but at a slower rate and with low blue flames over its surface. The mass loss rate of cellulose powder during combustion under free convection conditions was 0.08 g/s, which represented the linear portion of the mass loss data profile over 3 minutes (180 seconds). Figure 30 is a photograph and the mass loss-temperature profile of cellulose powder. As seen in the photograph, the thermocouple located 3 inches from the test platform was clearly in the flames directly above the pile. The drop or decrease in the temperature profile at ~320 seconds

occurred when the wire opened. Lower but sustained elevated temperatures at 3 inches and 6 inches above the pile from the low blue flames continued over the surface of the pile for an additional 500 seconds until the pile self-extinguished. Nearly all (93–96 wt%) of the combustible cellulose powder was consumed; the residual post-test residue was a fine, black soot. The FPA reaction-to-fire test data of cellulose powder was presented in Table 2; the peak heat release rate of dried cellulose powder was 0.87 kW (convective) and 2.10 kW (chemical).
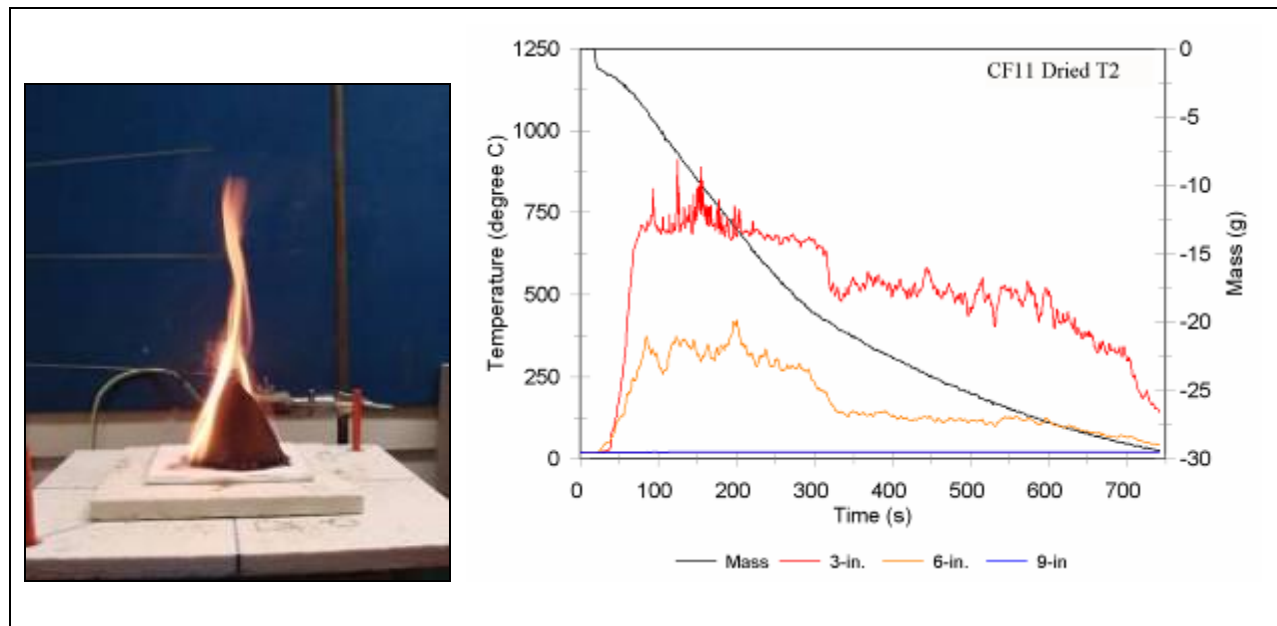
FIGURE 30. Representative photograph and mass loss-temperature profile of dried, cellulose powder.

The moisture content of cellulose powder had a negligible influence on the mass loss rate, duration of combustion, and peak temperature at 6 inches above the pile. Figure 31 compares the mass loss profiles of CF11 before and after drying at 108°C. There was no visual difference in the burning behavior with orange flames over the pile followed by low blue flames after the wire opened. The duration of visible flaming combustion of dried, cellulose powder was 692±37 seconds compared to 638±121 seconds for CF11 with 3.8wt% water. The dried cellulose powder had peak temperatures 6 inches from the test platform of 395±54°C; cellulose powder with 3.8wt% moisture had peak flame temperatures 358±71°C.

While moisture content did not have an influence on the burning rate or behavior of the fuel, the cellulose powder was dried before mixing with oxidizers to eliminate any potential influence of moisture content on the burning rate or behavior of the various oxidizers.
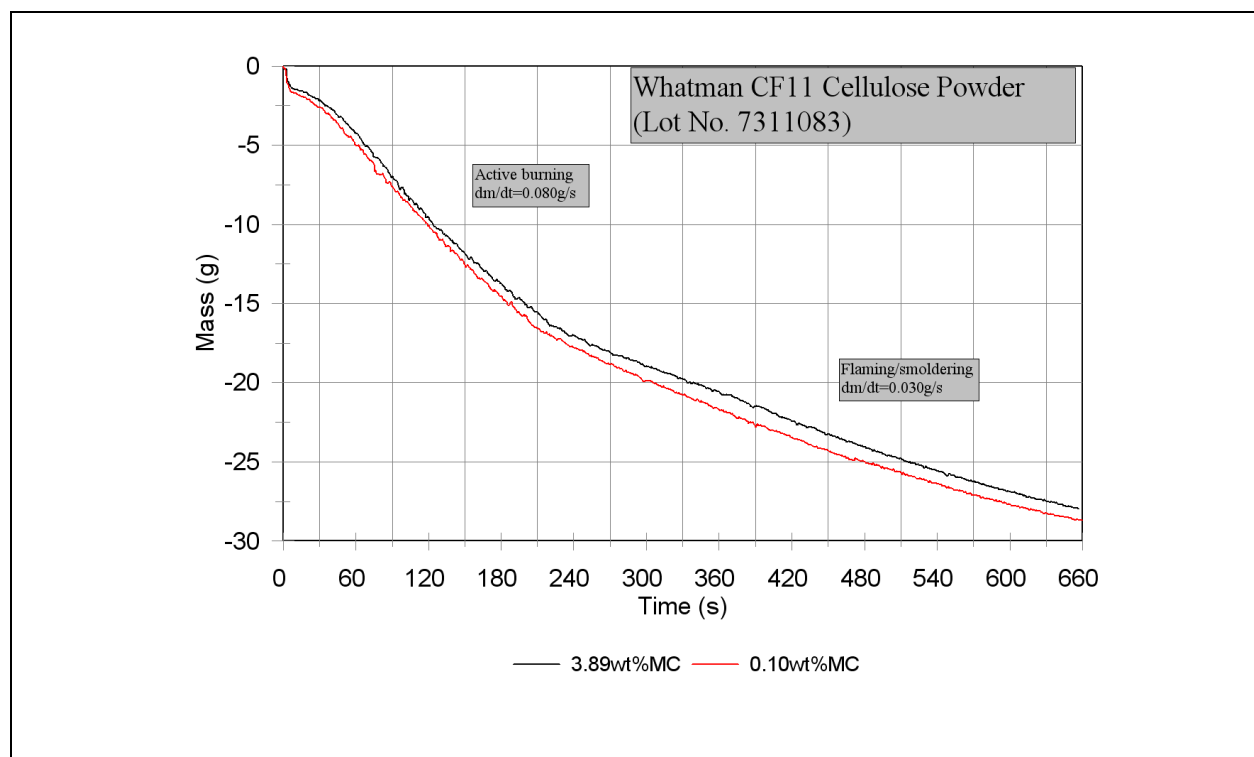
FIGURE 31. Comparing the mass loss profiles of cellulose powder as-received and after drying.

Sodium Chloride:Cellulose Powder Mixtures

Granular common salt (NaCl) did not increase the burning rate of cellulose powder; did not show glowing combustion; and, with increasing sodium chloride (NaCl) concentration, reduced the mass loss rate and peak temperature of the mixtures. Individual salt particles were apparent in the post-test residue. The mass loss rate of 1:1 sodium chloride:cellulose powder, from 20–80% cellulose powder consumed, was 0.045±0.006 g/s or one-half the mass loss rate of cellulose powder alone. The 1:1 mixture's calculated active burning time was 219±12 seconds, which was shorter than cellulose powder alone (e.g., less fuel). The peak temperature during combustion of the 1:1 mixture at 6 inches from the test platform was 167±6°C, which was lower than cellulose powder alone. At higher sodium chloride concentrations (4:1), the mass loss rate from 20–80% cellulose powder consumed was reduced to 0.021±0.002 g/s; the calculated active burning time was 251±6 seconds; and, the peak temperature at 6 inches from the test platform was 35±7°C (i.e., heat from the glowing wire). In the next section, the FPA combustion type tests with salt-cellulose powder mixtures resulted in lower peak convective and chemical heat release rates.

Oxidizer:Cellulose Powder Mixtures

Table 10 contains the data reduced from the bench-scale screening tests with 20 oxidizers, including pure oxidizers, formulated oxidizers, and oxidizers with intentional additives or diluents. The visual burning duration, mass loss rate, active burning time, time to 50% of the final measured mass, peak temperature at 6 inches above the test platform, and mass loss in Table 10 are shown as average values ± sample standard deviation over the number of trials performed in a series.

TABLE 10 Summary of Bench-Scale Screening Test Data

Oxidizer(Concentration)	Mix	Visual burning duration (s)	Mass loss rate* $_{20-80\%}$ (g/s)	Active burning time $_{0-80\%}$ (s)	Time to 50% consumed (s)	Tpeak @ 6-inches (°C)	Ignites Readily? (Y or N)	Mass Loss (%)	Peak Flame Height (in)
Magnesium peroxide complex (24-28%MgO₂)	1:1	313±18	0.091±0.004	227±8	150±5	175±29	Y	83±3	<9
	4:1	na	0.041±0.004	116±11	60±10	30±1	N	26±4	<3
Calcium hypochlorite with magnesium sulfate heptahydrate (50.8%Avail chlorine; 22% water)	1:1	301±53	0.12±0.02	126±15	72±6	205±86	Y	61±1	6
	4:1	104±11	0.17±0.03	68±4	50±10	99±20	N	44±4	<6
	9:1	na	0.14±0.01	83±4	54±5	41±3	N	41±4	nf
Potassium monopersulfate(45%)	1:1	284±27	0.06±0.01	205±15	86±9	157±21	N	65±5	6
	4:1	59±11	0.17±0.03	48±8	22±2	98±16	N	39±4	<6
Sodium persulfate (99%)	1:1	131±7	0.12±0.01	114±14	67±8	73±7	N	58±4	<6
	4:1	68±11	0.18±0.03	59±4	40±2	65±41	N	37±3	<3
	9:1	67±8	0.083±0.004	109±4	58±4	35±7	N	38±2	<3
Sodium dichlor dihydrate (99%)	1:1	160±22	0.19±0.02	111±1	73±2	201±41	N	81±2	6
	4:1	129±11	0.27±0.02	78±5	52±2	52±14	N	73±1	<3
	9:1	na	0.24±0.01	80±6	51±5	67±32	N	71±4	nf
Lithium hypochlorite (29%)	1:1	125±29	0.24±0.03	70±4	46±2	401±36	Y	55±2	9
	4:1	54±12	0.32±0.03	33±4	25±2	188±34	Y	31±1	6
	9:1	42±6	0.24±0.04	30±2	24±2	54±6	N	24±2	3
Barium nitrate (99%)	1:1	183±60	0.16±0.07	112±44	72±29	488±102	Y	65±2	6-9
	4:1	61±8	0.33±0.05	34±3	22±2	147±24	Y	44±1	3-6
	9:1	105±21	0.09±0.02	64±7	43±7	88±15	N	24±3	<3
1:1 by mass mixture calcium hypochlorite:sodium chloride	1:1	224±7	0.10±0.02	135±19	68±12	350±168	Y	56±4	6
	4:1	61±8	0.36±0.10	24±5	16±3	141±87	Y	32±2	<9
	9:1	33±5	0.31±0.15	22±5	14±2	108±31	Y	24±3	<6
Sodium percarbonate (99%)	1:1	144±14	0.22±0.01	84±3	50±4	385±75	N	70±3	9
	4:1	106±23	0.55±0.04	26±1	18±2	295±64	N	49±2	>6
	9:1	na	0.25±0.06	47±9	26±3	74±3	N	42±2	<3
Potassium bromate (99.8%)	3:7	84±10	0.62±0.07	39±4	27±2	968±124	Y	84±2	>9
Sodium perborate monohydrate (>96%)	1:1	67±6	0.48±0.03	37±3	23±2	940±83	Y	66±2	>9
	4:1	36±3	0.83±0.07	17±2	11±1	555±111	Y	51±2	9
Sodium nitrate (100%)	1:1	48±8	1.29±0.12	18±1	11±1	902±195	Y	84±2	>9
	4:1	36±3	0.58±0.08	17±3	8±1	65±12	N	37±3	<3

Oxidizer (Concentration)	Mix	Visual burning duration	Mass loss rate 20-80%	Active burning time 0-80%	Time to 50% consumed	Tpeak @ 6-inches	Ignites Readily?	Mass Loss	Peak Flame Height
		s	g/s	s	s	°C	Y or N	%	in
2:1 by mass mixture calcium hypochlorite:sodium chloride	1:1	171±21	0.20±0.03	71±8	38±1	363±24	Y	54±1	9
	4:1	39±8	1.39±0.04	9±1	7±1	741±164	Y	38±2	>9
	9:1	19±5	2.32±0.43	7±1	4±1	531±92	Y	34	9
Trichloroisocyanuric acid (99%)	1:1	117±10	0.55±0.04	40±2	18±1	323-418	Y	96±3	9
	4:1	8±2	2.45±0.67	15±2	11±1	93±28	Y	93±5	9
Potassium permanganate (>97.5%)	1:1	35±6	1.57±0.3	16±2	11±1	1138±78	Y	68±3	>9
	4:1	13±2	3.5±0.47	6±1	4±1	1005±73	Y	53±4	>9
Calcium peroxide(75%)	1:1	59±9	0.68±0.08	34±2	25±1	813±118	Y	70±3	>9
	4:1	16±3	4.35±1.52	8±1	6±1	236±45	Y	91±5	<6
Calcium hypochlorite (78.6%Avail Cl_2, 11.2% H_2O)	1:1	91±11	0.72±0.06	29±1	21±5	nr	Y	63±3	>9
	4:1	11±1	4.72±1.14	6±1	5±1	1215±72	Y	63±2	>9
Calcium hypochlorite (72.68%Avail Cl_2, 5.7% H_2O)	1:1	114±29	0.67±0.12	26±5	15±1	537±79	Y	59±2	>9
	4:1	8	8.6±1.8	5±1	4±1	429±28	Y	51±3	>9
	9:1	5±1	13.8±1.2	3±1	3±1	864±145	Y	48±2	>9
Potassium perchlorate (99%)	1:1	40	1.09±0.50	26±9	16±6	598±37	Y	89±2	>9
	4:1	8±1	9.59±1.49	6±1	5±1	1002±39	Y	87±5	>9
Sodium chlorate (99%)	1:1	10±1	4.78±0.75	5±1	4±1	563±150	Y	93±5	>9
	4:1	3	17.3±1.7	3±1	3±1	see text	Y	92±7	>9

Data shown as average±sample standard deviation. Nr= not recorded. Na=not applicable
* During combustion, the average mass loss rate of cellulose powder alone was 0.08g/s.

The mass loss rate from 20–80% ($MLR_{20-80\%}$) and active burning time (t_{active}) were strong indicators of burning rate. The bench-scale test data captured the range in burning rate of oxidizer-cellulose powder mixtures. The data in Table 10 show the $MLR_{20-80\%}$ mixtures ranged from 0.1 g/s to >10 g/s; the calculated active burning times ranged from 3–227 seconds; the time to 50% consumed ranged from ~1–155 seconds; the peak temperature at 6 inches ranged from 30°C (e.g., heat from the glowing wire) to over 1,000°C. Under the same test conditions, all oxidizers mixed with dried, cellulose powder had higher mass loss rates than the same amount of sodium chloride mixed with cellulose powder and exposed to the same ignition source.

Temperature data and peak flame height were also consistent with the observed burning behavior and added value to the mass loss test data. Specifically, the plume temperature data distinguished mass loss due to flaming combustion or decomposition with little to no flaming combustion. Similarly, the peak flame height distinguished between weak oxidizers with low flaming combustion and low peak flame height from strong oxidizers with flames extending greater than 9 inches from the test platform. The temperature profiles provided an indication of the mixture's ignition propensity. Oxidizer-cellulose powder mixtures that ignited readily and spread flaming combustion over the pile showed a higher initial rate in temperature rise (i.e., dT/dt) and higher temperatures at 6 inches above the test platform. Oxidizer-cellulose powder mixtures that did not ignite readily and spread discoloration with or without flaming combustion had temperature profiles with slower or lower initial rates of temperature rise and lower peak temperatures at 6 inches above the test platform. The sodium chlorate-cellulose powder mixtures were instantly ignited and burned so vigorously and rapidly that accurate temperature data, even at 0.2 second intervals, was difficult to capture.

The correlation between visual burning behavior and the test data is illustrated with photographs and figures from screening tests with 9-g potassium bromate (99.8%) and 21-g cellulose powder. Potassium bromate is listed as typical under Class 3 oxidizers. The 3:7 mixture is used in UN Test O.1 as the reference oxidizer-mixture for the lowest hazard Packing Group III assignment.

The 3:7 oxidizer-cellulose powder mixture ignited readily; the peak flame height during combustion reached and was sustained at greater than 9 inches from the test platform (Fig. 32). The mixture showed intermittent, low flaming near the end of the test, but flaming combustion was over in less than 100 seconds. The 3:7 mixture showed consistent burning behavior (e.g., repeatability) as demonstrated by the mass loss profiles compiled in Figure 33. The average mass loss rate from 20–80% consumed was 0.62±0.07 g/s. Figure 34 is a representative mass loss-temperature profile, which includes labels and arrows to indicate the mass of the mixture at 20% and 80%. The indicated mass at 20% and 80% lie within the elevated temperature profile envelope and does not include intermittent or irregular burning observed at/near the end of test. The presence of intermittent or low flaming combustion appears as elevated temperatures at 3 inches above the test platform in Figure 34. In UN Test O.1, intermittent flames cause difficulty for test operators with stopwatches to determine the end of the main reaction including mixtures with the reference oxidizer. Temperatures in the plume above the fuel-rich, potassium bromate pile exceeded 1,000°C.

**FIGURE 32. Photograph during screening test with 30 g,
3:7 potassium bromate:cellulose powder.**

3:7 KBrO$_3$ (99.8%)
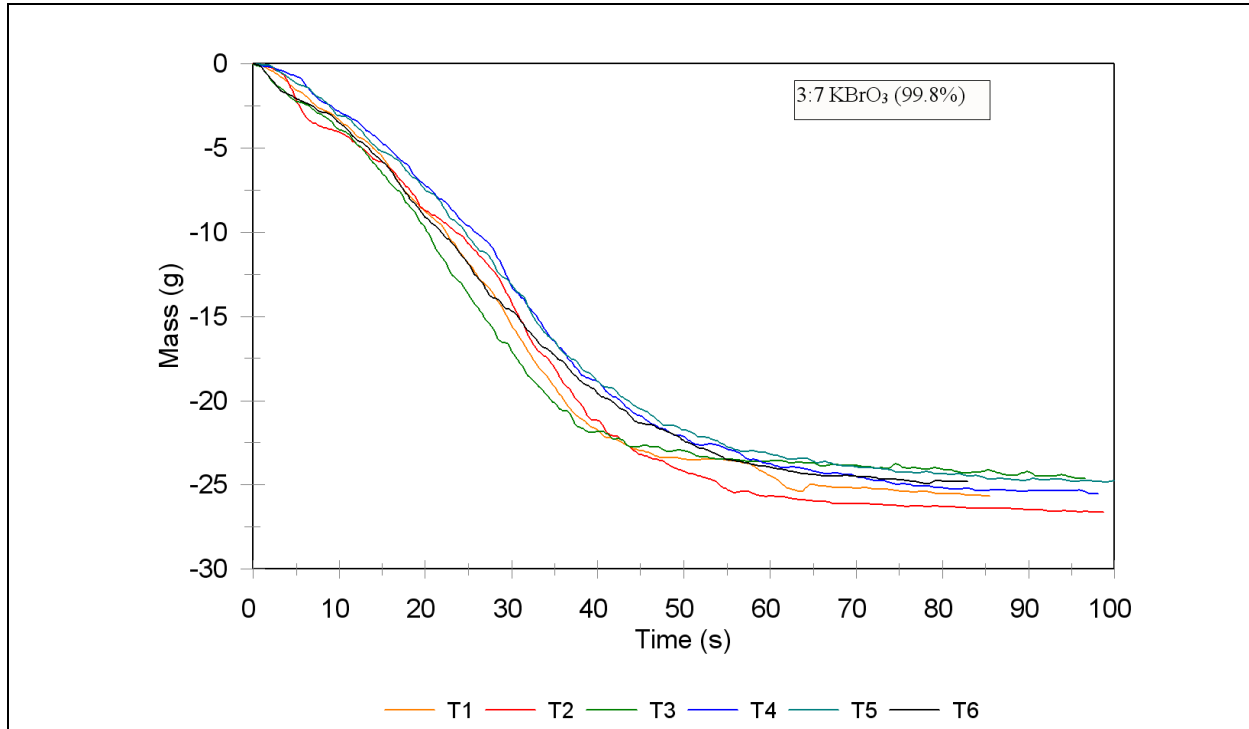
FIGURE 33. Mass loss profiles from six trials with 30-g 3:7 potassium bromate:cellulose powder mixtures.
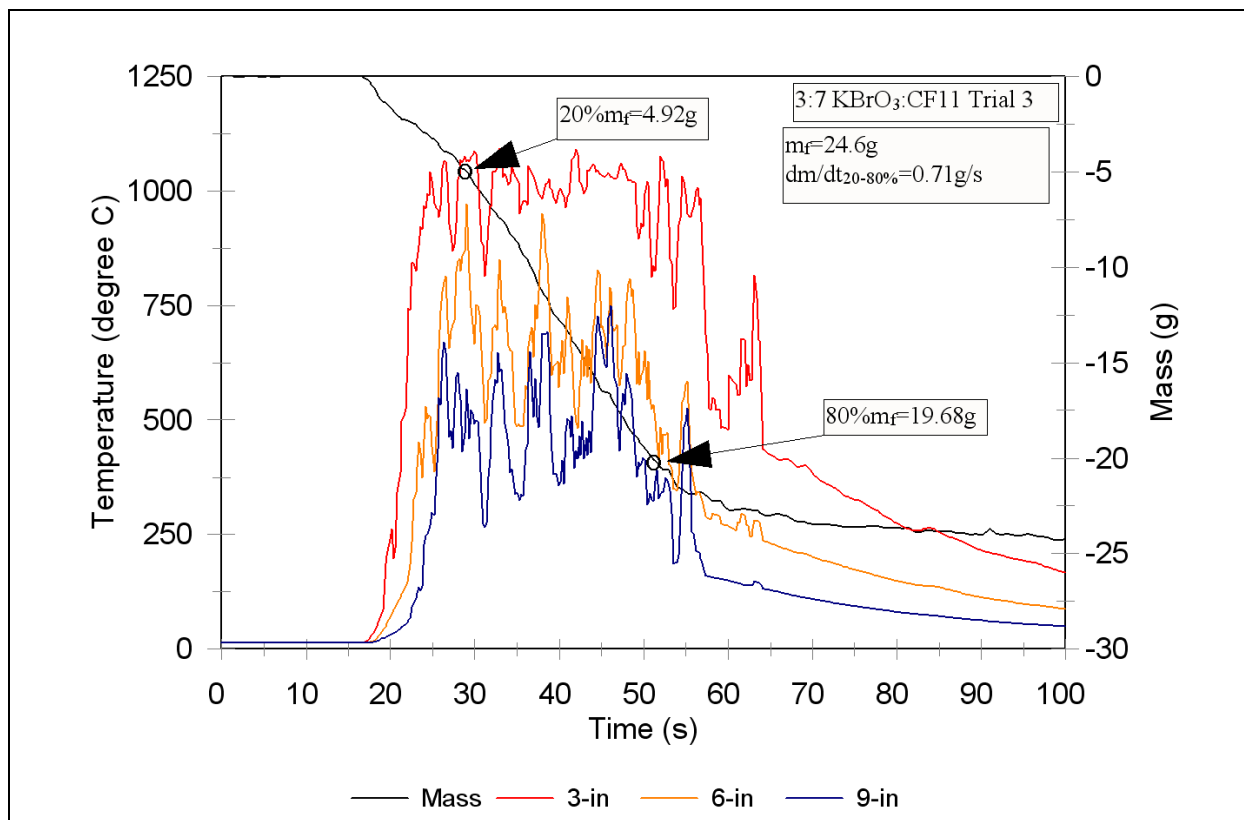
**FIGURE 34. Representative mass loss-temperature profile from one trial
with 3:7 potassium bromate:cellulose powder.**

Other oxidizers were slow to ignite and spread discoloration over the pile instead of flames. As expected, mixtures that underwent dehydration and/or decomposition when exposed to the glowing wire also resulted in some mass loss. Temperature data from the thermocouples above the pile distinguished mixtures that underwent dehydration and/or decomposition with little to no or low flaming combustion from mixtures that burned with flames extending from the test platform. To illustrate mass loss and low temperature during decomposition with minor flaming combustion, Figure 35 contains a photograph and the mass loss-temperature profile of sodium dichloroisocyanurate dihydrate mixed in equal parts (30g, 1:1) with cellulose powder. This mixture was slow to ignite, released white gaseous products throughout the test, had little and low flaming combustion, and spread black discoloration over the pile. The average mass loss rate was 0.2 g/s, the duration of decomposition was 111 seconds, and the total mass lost was 24 grams or 81wt%. The peak temperature immediately above the pile was only ~300°C.
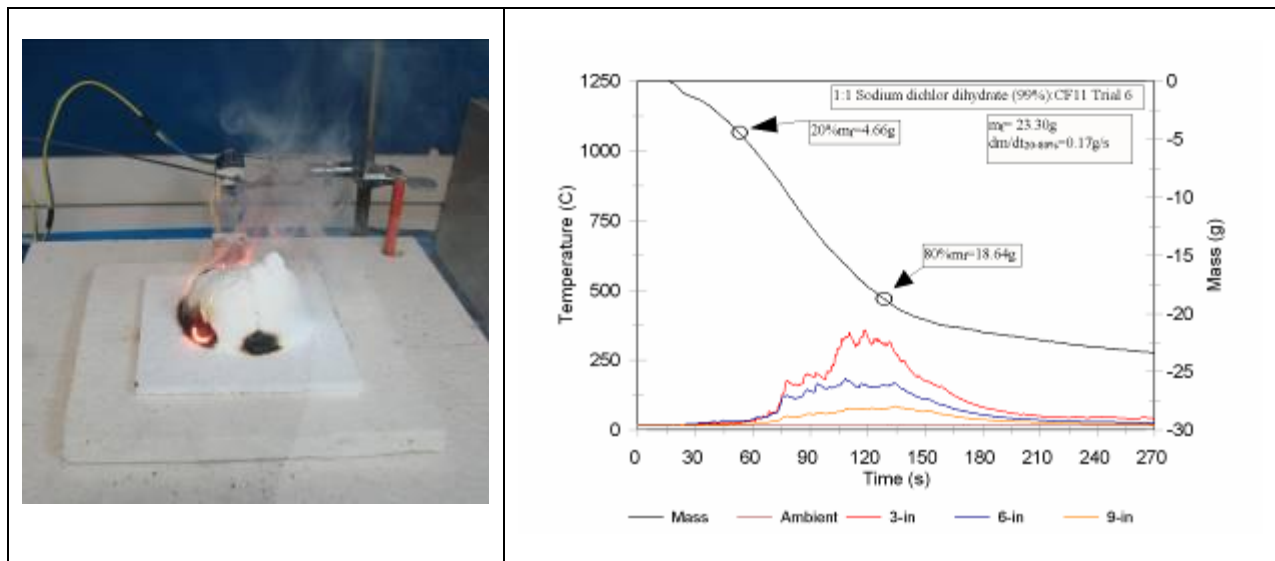
FIGURE 35. Photograph and mass loss-temperature profile during screening test with sodium dichlor dihydrate.

The correlation between mass loss rate and active burning time from the various oxidizer-cellulose powder mixtures in 1:1 and 4:1 by mass mixtures are illustrated with scatter plots in Figures 36 and 37, respectively. The relationship between mass loss rate and burning time is not linear but follows a power law equation.
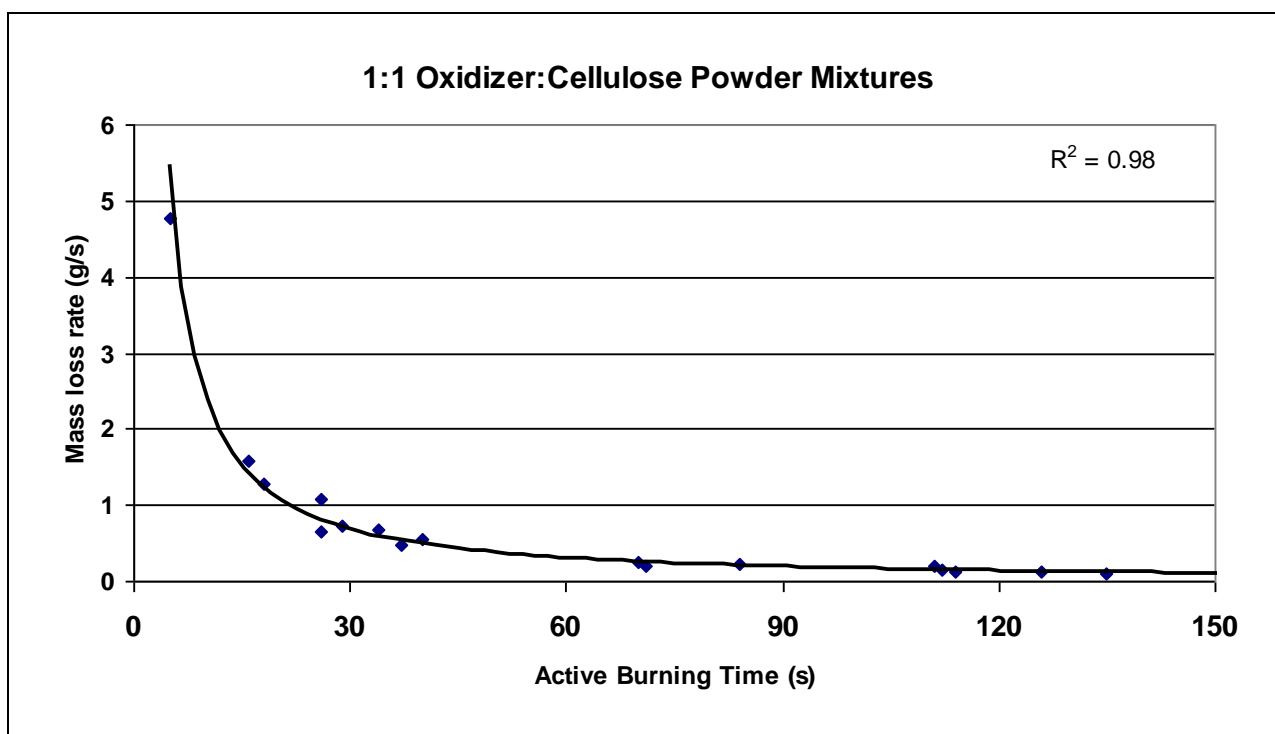
FIGURE 36. Correlation between mass loss rate and active burning time for 1:1 oxidizer:cellulose powder mixtures.
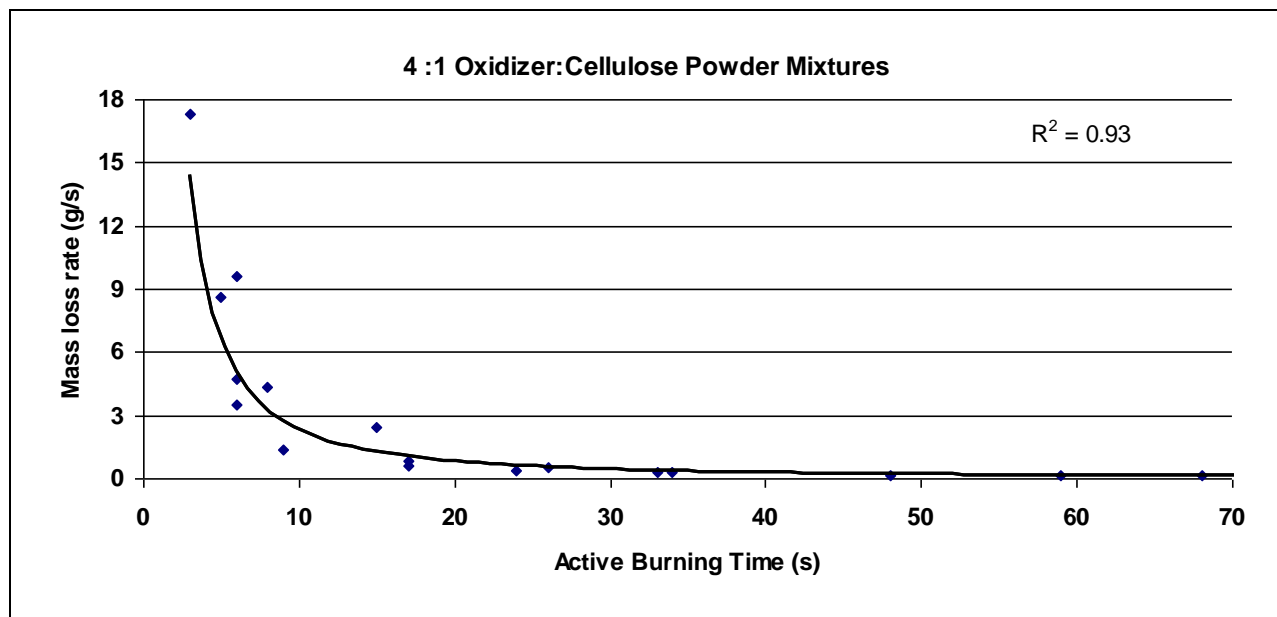
FIGURE 37. Correlation between mass loss rate and active burning time for 4:1 oxidizer:cellulose powder mixtures.

Oxidizers may increase the intensity of a fire either in the condensed phase, in the gaseous phase above the burning material, or both. Further, burning rate is concentration-dependent. The relationship between oxidizer (and fuel) concentration and burning rate are integral to existing tests that evaluate the burning rate of various oxidizer-combustible fuel mixtures. It is well known that the burning behavior of oxidizers is a function of the amount of fuel or fuel content. The historic Bureau of Mines[19] and GE Research[20] studies tested numerous mixtures of the oxidizer and fuel (i.e., sawdust), in 10wt% increments. The ratio of oxidizer and fuel with the fastest propagation rate was reported. UN Test O.1 includes five different mixtures: 3:7, 2:3, and 3:2 potassium bromate:cellulose powder and 1:1 and 4:1 by mass mixtures of the test oxidizer with dried cellulose powder. The influence of composition is clearly demonstrated by specific mixtures used for pyrotechnic effects, explosions, and smoke powders.

A number of the 1:1 by mass mixtures of oxidizer and finely divided cellulose powder had higher flames, higher peak temperatures, longer durations of burning, but lower or slower mass loss rates than the 4:1 mixtures. Mass loss rate data alone does not capture this burning behavior which presents its own fire hazard. Other oxidizers exhibited accelerated burning behavior with increasing oxidizer concentration with concurrent faster mass loss rates. Figure 38 illustrates the first case using photographs and mass loss-temperature profiles from the screening tests with barium nitrate. Figure 39 illustrates the second behavior with calcium hypochlorite. The 1:1 by mass barium nitrate:cellulose powder mixture had higher flames, higher peak temperatures, and longer burning durations than the 4:1 by mass mixture. The oxidizer-rich 9:1 by mass barium nitrate:cellulose powder mixture exhibited only minor combustion with low flames, and the mixture phase changed from a crystalline solid into a boiling slurry. In other words, the oxidizer clearly contributed to increasing the burning rate of cellulose powder when mixed in equal parts but the oxidizer-rich mixture mostly decomposed. When comparing the different barium nitrate:cellulose powder mixtures' mass loss rates, the maximum mass loss rate occurred during combustion of the 4:1 mixture and the 1:1 mixture mass loss rate was intermediate between the 4:1 and 9:1 mixture mass loss rates. On the other hand, the mass

loss rate increased and the burning time decreased with increasing oxidizer concentration in the calcium hypochlorite:cellulose powder mixtures. The mass loss and temperature profiles from the calcium hypochlorite-cellulose powder mixtures are clearly different from barium nitrate-cellulose powder mixtures.
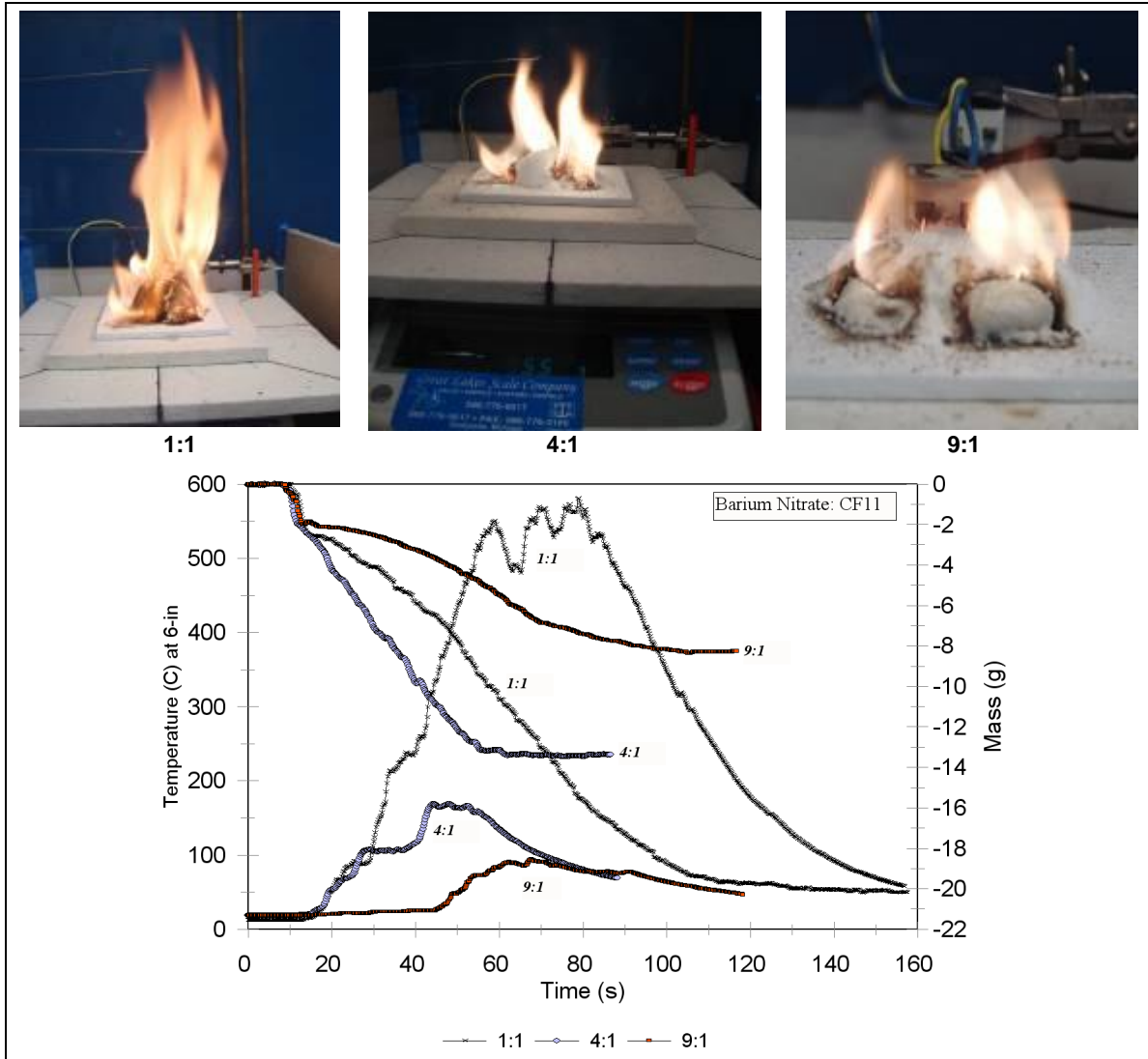
FIGURE 38. Representative photographs and mass loss-temperature profiles of 1:1, 4:1 and 9:1 mixtures of barium nitrate:cellulose powder (30-g)

**FIGURE 39. Representative photographs and the mass loss-temperature profiles of
1:1, 4:1 and 9:1 high-strength calcium hypochlorite:cellulose powder (30-g)**

Like barium nitrate, oxidizer-cellulose powder mixtures that had higher flame height and longer burning durations when mixed in equal parts (i.e., 1:1) with dried cellulose powder but lower mass loss rates than the 4:1 or 9:1 concentrations were calcium hypochlorite formulated with magnesium sulfate heptahydrate, potassium monopersulfate, sodium persulfate, sodium dichloroisocyanurate dihydrate, lithium hypochlorite, sodium perborate monohydrate, sodium nitrate, sodium percarbonate, 1:1 calcium hypochlorite-sodium chloride, and calcium peroxide. Like calcium hypochlorite, oxidizer-cellulose powder mixtures that exhibited peak flame heights at or above 9 inches for all mixtures and mass loss rates that increased with increasing oxidizer concentration were 2:1 calcium hypochlorite-sodium chloride, potassium permanganate, high-strength calcium hypochlorite with low- and high-water content, potassium perchlorate, and sodium chlorate. Trichlor principally decomposed when exposed to the glowing wire; the rate of

decomposition increased with increasing trichlor in the mixtures. By inspection of the data in Table 10, a majority of oxidizers tested had the fastest or maximum mass loss rate at the 4:1 oxidizer:cellulose powder by mass mixtures.

The mass loss rates and active burning times of the 4:1 oxidizer-cellulose powder mixtures are shown for the various oxidizers in Figure 40. The data demonstrate the range in burning behavior. The trend in Figure 40 shows that oxidizer mixtures with low mass loss rates typically had long active burning times and oxidizers with high mass loss rates had short active burning times.
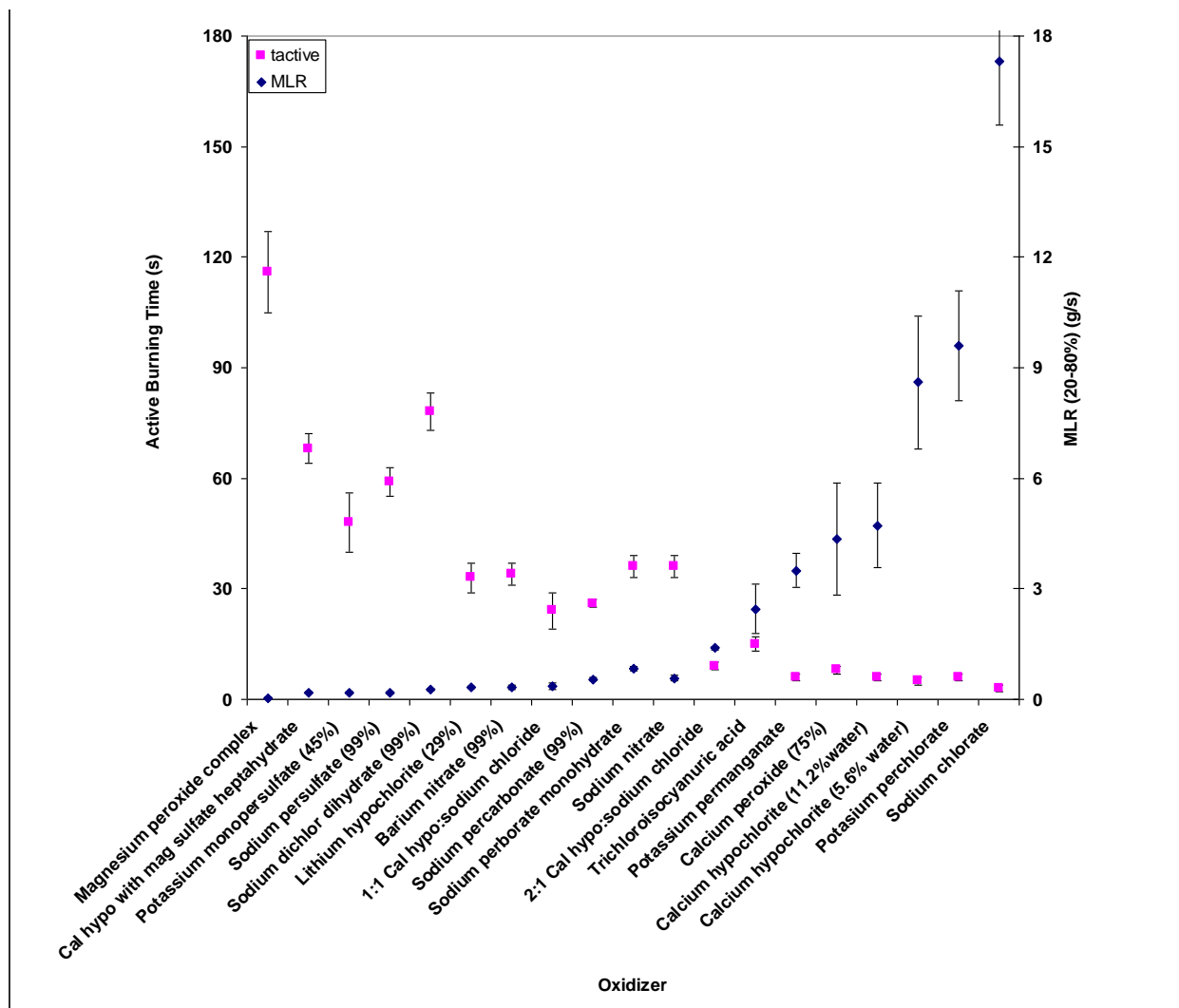
FIGURE 40. Active burning time and mass loss rate
from 20% to 80% consumed for 19 oxidizers in 4:1 mixtures with cellulose powder

The screening test distinguished between pure and formulated oxidizers and, in one case, an oxidizer with low- and high-water content. The 2:1 by mass calcium hypochlorite-sodium chloride admixture had a higher mass loss rate and shorter burning time than the 1:1 calcium hypochlorite-sodium chloride admixture and a lower mass loss rate and longer active burning

time than high-strength calcium hypochlorite. Similarly, the calcium hypochlorite with magnesium sulfate heptahydrate had lower mass loss rate and longer active burning time than high-strength calcium hypochlorite. The water content of calcium hypochlorite can vary. The bench-scale screening test was able to distinguish between a calcium hypochlorite with 5.6% water and 11.2% water. The mass loss rate of the former was 8.6 g/s compared to 4.7 g/s; their active burning times were about the same (i.e., 6s). In a similar manner, the bench-scale screening test can be used to investigate the influence of particle size and size distribution on the burning rate.

Fire Propagation Apparatus Test Results

Combustion-type tests using the Fire Propagation Apparatus were first performed by FM Global in the late 1990s as part of a project to evaluate the criteria for packing group assignment for the transportation of commercial solid oxidizers. Instead of burning time, the energy released at eighty percent the total heat released based on carbon dioxide generation was proposed as criteria. An alternate burning time was proposed, not based on stopwatch time, but on the time from the first measurable mass loss to 80% of the mixture consumed. These tests involved various granular oxidizers mixed with dried sawdust and ignited with a glowing wire. This preliminary work showed a range in the duration of burning, the peak mass loss rate, heat release rate and total heat released for the various oxidizers.

While it provides far more and valuable fire test response data, including the peak heat release rate and total heat released, the FPA is not widely available for use to screen and assign oxidizers to a NFPA Class. For this project, the FPA was used to validate the screening test. The same behavior observed during the bench-scale screening tests with cellulose powder, sodium chloride (NaCl)-cellulose powder mixtures, and oxidizer-cellulose powder mixtures were observed when using the FPA. Oxidizer-fuel mixtures slow to ignite and spread flame in bench-scale testing were slow to ignite and spread flame during the FPA tests. Oxidizer-fuel mixtures that ignited readily and burned rapidly in the bench-scale tests were similarly observed to ignite readily and burn rapidly during the FPA tests. Oxidizer-fuel mixtures that did not ignite but spread discoloration and/or had low flame showed the same behavior in the FPA tests. Oxidizer-fuel mixtures that generated significant gaseous products were also observed to generate significant gaseous products in the FPA. The only difference was that under forced convection conditions, the mass loss rate was higher and the active burning time shorter than the same mixtures tested under free convection conditions at the bench-scale test.

The FPA tests with oxidizer-cellulose powder mixtures provided calorimetric or heat release rate data not provided by the bench-scale screening test—though both record the change in mass over time. In general, the peak mass loss rate during combustion occurred at the same time as the peak heat release rate and, higher peak mass loss rates corresponded to higher peak heat release rates. The additional data corroborated the observed dependence of oxidizer concentration on the burning intensity of the various mixtures with dried cellulose powder. Like the bench-scale screening test, the FPA heat release rate data distinguished between (1) weak oxidizers, oxidizers that principally decomposed, and strong oxidizers; (2) pure and formulated oxidizers; and (3) oxidizers with different water content.

The FPA test data are summarized in Tables 11–14 for cellulose powder, cellulose powder-sodium chloride (NaCl) mixtures, 30-g oxidizer:cellulose powder mixtures, and 15-g oxidizer:cellulose powder mixtures, respectively. Fifteen gram mixtures were tested when ignition of the mixture was expected to produce flames that extended from the test platform to the opening of the exhaust collection duct; flame extension into the duct would result in invalid

test data. The test data in Tables 11–14 include duration of visible flaming combustion (determined from video recordings of each test), peak mass loss rate[††], peak convective heat release rate (HRR_{conv}), peak heat release rate based on carbon dioxide generation (HRR_{CO2}), time to peak convective heat release rate, and effective heat of combustion calculated from the total energy (kJ) released divided by the total mass of material consumed.

Seven trials were performed with 30-g cellulose powder. The mass loss rate was comparable to the screening test. The average chemical heat release rate based on oxygen consumption and gas temperature rise was 1.8 kW; the average heat release rate based on carbon dioxide generation was 2 kW. The convective heat release rate was 42–48% of the heat release rate based on carbon dioxide generation. The effective heat of combustion of cellulose powder, based on the total heat released, was 19.2±0.4 kJ/g. Moisture content (up to 3.8 wt%) had a negligible effect on the heat release rate.

Similar to the bench-scale screening tests, sodium chloride (NaCl) did not increase or contribute to the burning rate of cellulose powder. The mixtures were slow to ignite and spread flaming combustion, and the peak mass loss rate and peak heat release rates were less than cellulose powder alone. Increasing the amount of sodium chloride (NaCl) resulted in even lower mass loss rates and lower peak heat release rates. The peak chemical heat release rate of 1:1 by mass sodium chloride (NaCl)-cellulose powder mixture ranged from 1.3–1.5 kW; the peak convective heat release rate ranged from 0.5–0.6 kW. The peak convective and chemical heat release rates of the 4:1 sodium chloride (NaCl)-cellulose powder mixtures were lower than the 1:1 mixtures.

[††] The FPA software calculates the mass loss rate using a moving linear regression of data over 18 seconds.

TABLE 11. Cellulose Powder FPA Test Data

Moisture Content (%)	Visual Burning Duration (s)	Peak MLR (g/s)	Peak HRR$_{conv}$ (kW)	Peak HRR$_{CO2}$ (kW)	Time to Peak HRR (s)
3.8	722, 772	0.09	0.73, 0.84	1.7, 1.87	155, 198
0.45*	713±59	0.10	0.87±0.08	2.10±0.11	138±20

Five trials shown as average ± sample standard deviation.

MLR=mass loss rate; HRR=heat release rate

TABLE 12. Sodium Chloride-Cellulose Powder Mixture FPA Test Data

Mixture (Mass)	Visual Burning Duration (s)	Peak MLR (g/s)	Peak HRR$_{conv}$ (kW)	Peak HRR$_{CO2}$ (kW)	Time to Peak HRR (s)	Effective Heat of Combustion (kJ/g)*
1:1 (30-g)	464	0.07	0.55	1.4	101	14
1:1 (30-g)	404	0.09	0.60	1.3	140	20
1:1 (15-g)	185	0.08	0.52	1.5	67	18
4:1 (30-g)	235	0.04	0.33	0.88	129	13
4:1 (30-g)	226	0.06	0.30	0.68	139	14
4:1 (15-g)	142	0.03	na	0.57	na	14
9:1 (30-g)	284	--	0.25	0.37	224	--

*MLR=mass loss rate; HRR=heat release rate. * Using the total heat released based on carbon dioxide generation and the amount of material consumed.*

TABLE 13. Oxidizer-Cellulose Powder (30 g) Mixture FPA Test Data

Oxidizer (Concentration)	Test Mixture Ox:CF11	Visual Burning Duration s	Peak MLR g/s	Peak HRR$_{conv}$ kW	Peak HRR $_{CO2}$ kW	Time to Peak HRR$_{conv}$ s	Effective Heat of Combustion (kJ/g)*
Sodium dichloroisocyanurate dihydrate (99%)	1:1	96	0.42	0.7	2.4	56	6.5
	4:1	70	0.39	0.4	2.2	44	5.7
Sodium percarbonate (30-40%)	1:1	248	0.10	0.6	1.6	108	14
	4:1	270	0.06	0.3	0.7	175	6.9
Barium nitrate (99%)	1:1	121	0.30	1.9	4.9	56	15
	4:1	40	0.58	1.4	3.6	17	6.0
	9:1	85	0.10	0.7	1.9	17	--
Sodium persulfate (99%)	1:1	118	0.15	0.5	1.5	73	5.8
	4:1	105	0.25	0.3	1.4	30	4.8
	9:1	71	0.15	0.2	1.0	60	4.0
Lithium hypochlorite (29%)	1:1	122	0.22	1.1	3.2	38	15
	4:1	37	0.42	0.5	2.4	12	5.0
	9:1	48	0.35	0.3	1.5	25	2.1
Trichloroisocyanuric acid (99%)	1:1	76	1.13	4.4	14	9	9.4
70:30 Calcium hypochlorite(50.87%Avail. chlorine, 22% water): magnesium sulfate heptahydrate	1:1	367	0.69	0.6	1.5	79	11
	4:1	89	0.29	0.5	1.6	49	4.0
	9:1	na	0.19	0.2	0.5	26	--
1:1 Calcium hypochlorite:NaCl (33% avail. chlorine)	1:1	197	0.15	0.7	1.9	49	14
	4:1	133	0.39	1.0	3.1	23	11
	9:1	35	0.30	0.6	1.8	18	5.7
Potassium perchlorate (99%)	1:1	150	1.04	2.7	12	8	9.9
2:1 Calcium hypochlorite:NaCl (48% avail. chlorine)	1:1	172	0.19	1.4	3.7	29	14
	4:1	30	0.53	2.6	9.0	10	6.1
Calcium hypochlorite (78.6% avail. chlorine, 11.2% water)	1:1	100	0.74	2.5	7.4	10	13
Calcium hypochlorite (72.68% avail. chlorine, 5.7% water)	1:1	88	0.55	2.9	9.9	11	12

*na-no flaming combustion observed. * Using the total heat released based on carbon dioxide generation and the amount of material consumed.*

TABLE 14. Oxidizer-Cellulose Powder (15g) Mixture FPA Test Data

Oxidizer (Concentration)	Test Mixture Ox:CF11	Visual Burning Duration s	Peak MLR g/s	Peak HRR$_{conv}$ kW	Peak HRR$_{CO2.}$ kW	Time to Peak HRR s	Effective Heat of Combustion (kJ/g)*
Calcium peroxide (75%)	1:1	82	0.47	2	6.9	19	15
	4:1	12	na	2	5.4	5	na
Trichloroisocyanuric Acid (99%)	1:1	96	0.45	2	8.8	8	9.5
	4:1	13	1.00	0.7	3.6	10	3.3
Potassium permanganate (>97.5%)	1:1	33	0.61	2.4	9.4	5	12
	4:1	9	0.83	1.4	6.4	4	5.3
Potassium perchlorate (99+%)	1:1	145	0.44	1.6	7.0	6	12
	4:1	9	0.86	2.5	11	3	7.3
Calcium hypochlorite (78.6% avail. chlorine, 11.2% water)	4:1	7	0.71	2.4	7.4	7	6.3
Calcium hypochlorite (72.68% avail.chlorine, 5.7% water)	4:1	11	0.80	2.4	7.6	10	5.7

na-mass loss rate data not valid due to stuck bearing on load cell shaft
* Using the total heat released based on carbon dioxide generation and the amount of material consumed.

From Tables 12, 13 and 14, the peak mass loss rate and peak heat release rate of a majority of the oxidizers were greater than the mixtures with the equivalent amount of sodium chloride. Figure 41 shows the peak heat release rate occurred at or near the peak mass loss rate during combustion of the oxidizer-cellulose powder mixtures. The peak convective heat release rate and the effective heat of combustion were higher for the oxidizer-cellulose powder mixtures that had higher flame extension from the pile.

The influence of burning behavior as a function of oxidizer and fuel content from the bench-scale screening test data was illustrated with barium nitrate. The results showed that the 1:1 by mass mixture of barium nitrate and cellulose powder had higher flames, higher peak temperatures, and slower mass loss rate than the 4:1 mixture. The heat release rate profiles of barium nitrate:cellulose powder mixtures are shown in Figure 42. The FPA heat release rate results are consistent with the observed difference in burning intensity of the three mixtures.

The peak heat release rates of 1:1 oxidizer-cellulose powder mixtures were higher than the 4:1 mixtures for eight oxidizers: sodium persulfate, calcium hypochlorite formulated with magnesium sulfate heptahydrate, formulated sodium percarbonate, sodium dichlor dihydrate, lithium hypochlorite (29%), barium nitrate, potassium permanganate, and trichlor. With the exceptions of potassium permanganate and trichlor, the peak heat release rates based on carbon dioxide generation of the oxidizers in 30 gram mixtures were less than 3 kW. The peak convective heat release rates of the 4:1 mixtures were higher than the 1:1 mixtures for five oxidizers: 2:1 calcium hypochlorite-sodium chloride (NaCl), calcium peroxide (75%), potassium perchlorate, calcium

hypochlorite with low-water content, and calcium hypochlorite with high-water content. These materials had peak heat release rates based on carbon dioxide generation greater than 3 kW.
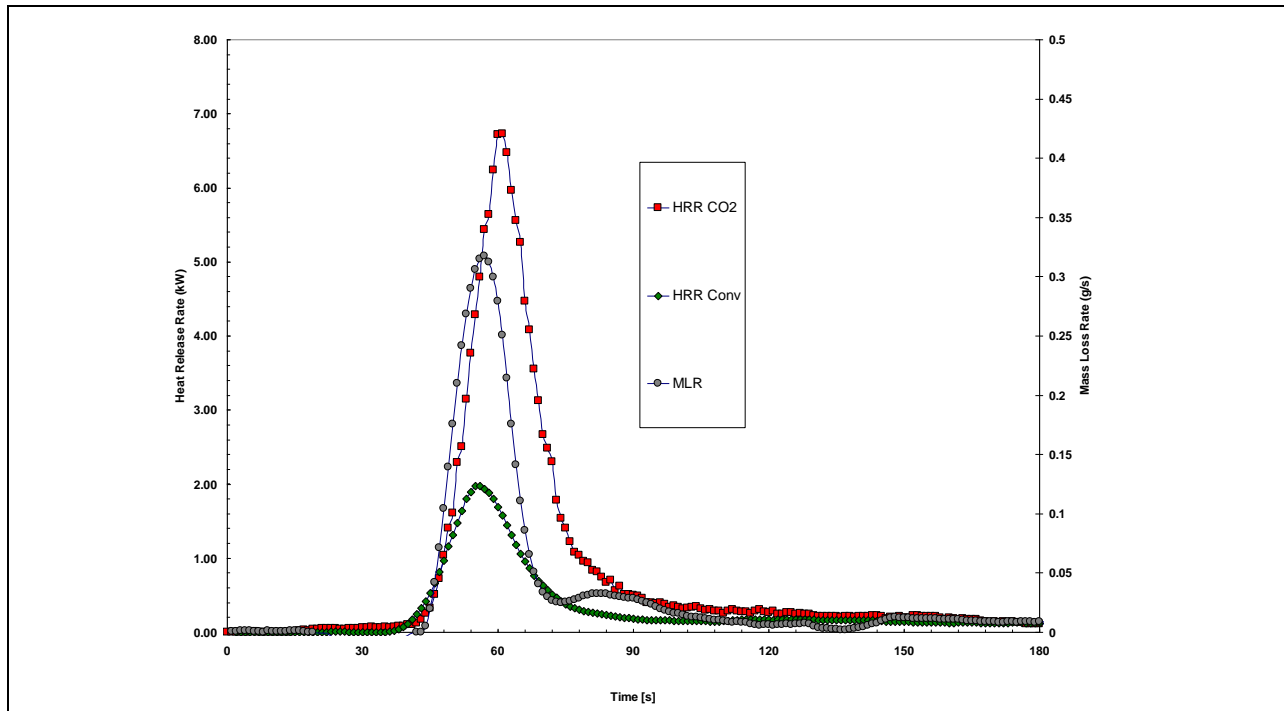
FIGURE 41. Heat release rate and mass loss profile of 1:1 calcium peroxide (75%):cellulose powder (15 g) showing the correlation between the time to the peak heat release rate and peak mass loss rate.
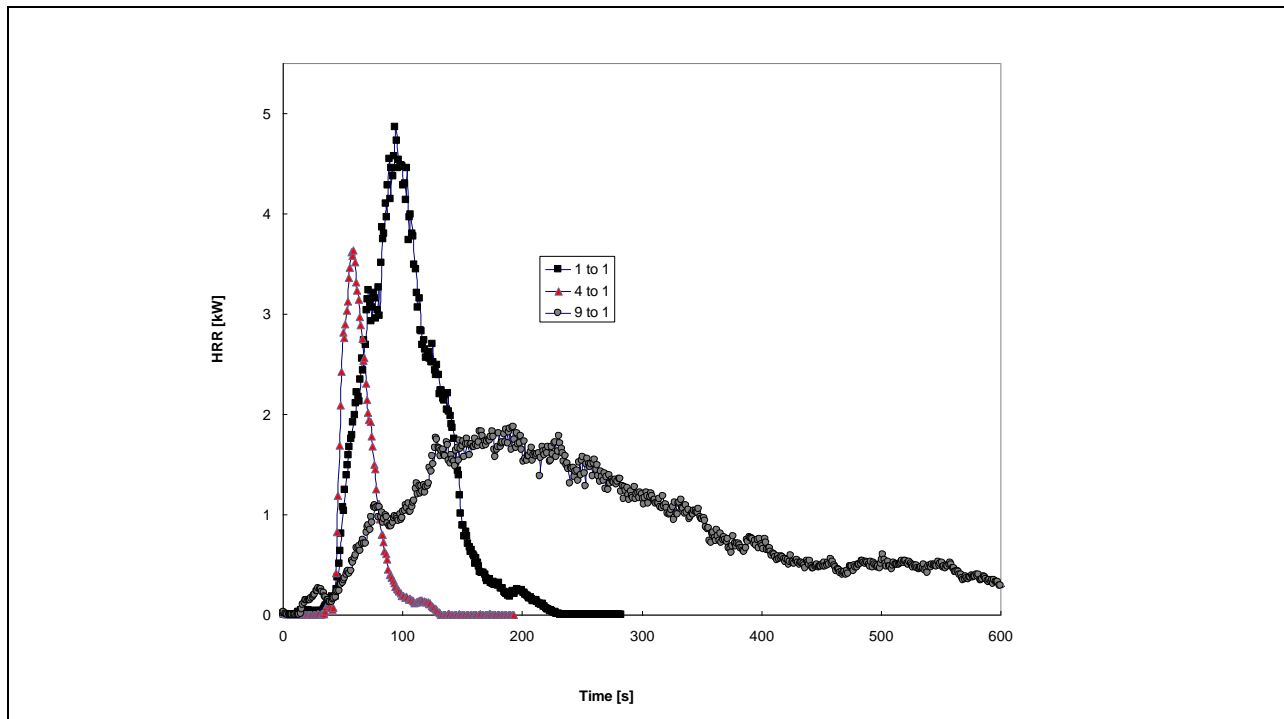
FIGURE 42. Barium nitrate:cellulose powder mixture heat release rate profiles illustrating the difference in burning behavior as a function of oxidizer concentration.

The influence of oxidizer concentration on the heat release rate are shown in Figure 43 using the HRR profiles of 1:1 mixtures of high-strength calcium hypochlorite, 2:1 calcium hypochlorite-sodium chloride (NaCl), 1:1 calcium hypochlorite-sodium chloride (NaCl), and sodium chloride (NaCl) with cellulose powder. This figure perfectly captures the range in burning behavior and burning rate.   Increasing oxidizer concentration resulted in an increased burning rate, as characterized by higher peak heat release rates and shorter times to peak heat release rate. The peak heat release rate of high-strength calcium hypochlorite was reduced 62% in the 2:1 mixture and 81% in the 1:1 mixture. The formulation of calcium hypochlorite with a hydrated salt (not shown) reduced the oxidizer's peak heat release rate based on carbon dioxide by 85% (from 9.9-kW to 1.5-kW). The same approach can be used to study the influence of different additives or diluents on the burning rate of any oxidizer.
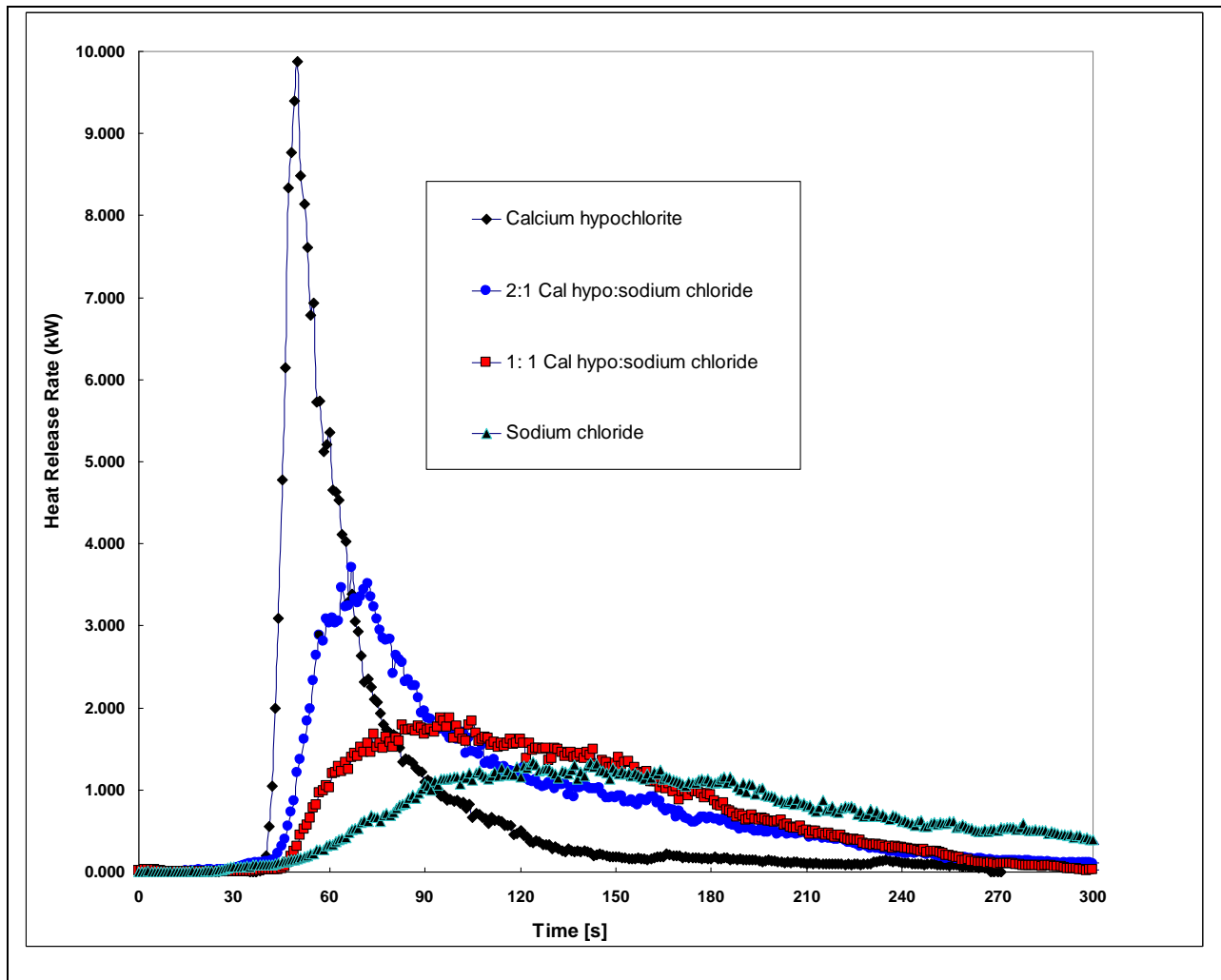
FIGURE 43. Heat release rate profiles of calcium hypochlorite, calcium hypochlorite-sodium chloride and sodium chloride (NaCl):cellulose powder mixtures (1:1, 30 g).

Under the FPA conditions, the peak heat release rate based on carbon dioxide generation showed a better correlation with mass loss rate and the observed burning behavior than the peak convective heat release rate. The peak heat release rate (HRR) and peak mass loss rate

(MLR) of cellulose powder and 30 gram mixtures of 1:1 sodium chloride (NaCl): cellulose powder and 1:1 inorganic oxidizer:cellulose powder are shown in Figure 44. None of the oxidizers in Figure 44 contain carbon in their chemical structure or as a major constituent; the main source of carbon is cellulose powder. Compared to the same quantity of sodium chloride in the mixture with cellulose powder, all oxidizers had higher heat release rates and therefore increased the burning rate of cellulose powder. The peak heat release rate depended on the type of oxidizer, ranging from 1.5 kW for sodium persulfate with minor flaming combustion to 12.3 kW for potassium perchlorate, which burned vigorously. Potassium perchlorate and calcium hypochlorite burned intensely at the test platform. The lower peak convective heat release rate for these oxidizers compared to their peak chemical heat release rate is interpreted as an indicator of an accelerated rate of combustion with higher temperatures at the test platform. Higher temperatures result in a greater fraction of the energy being released as thermal radiation.
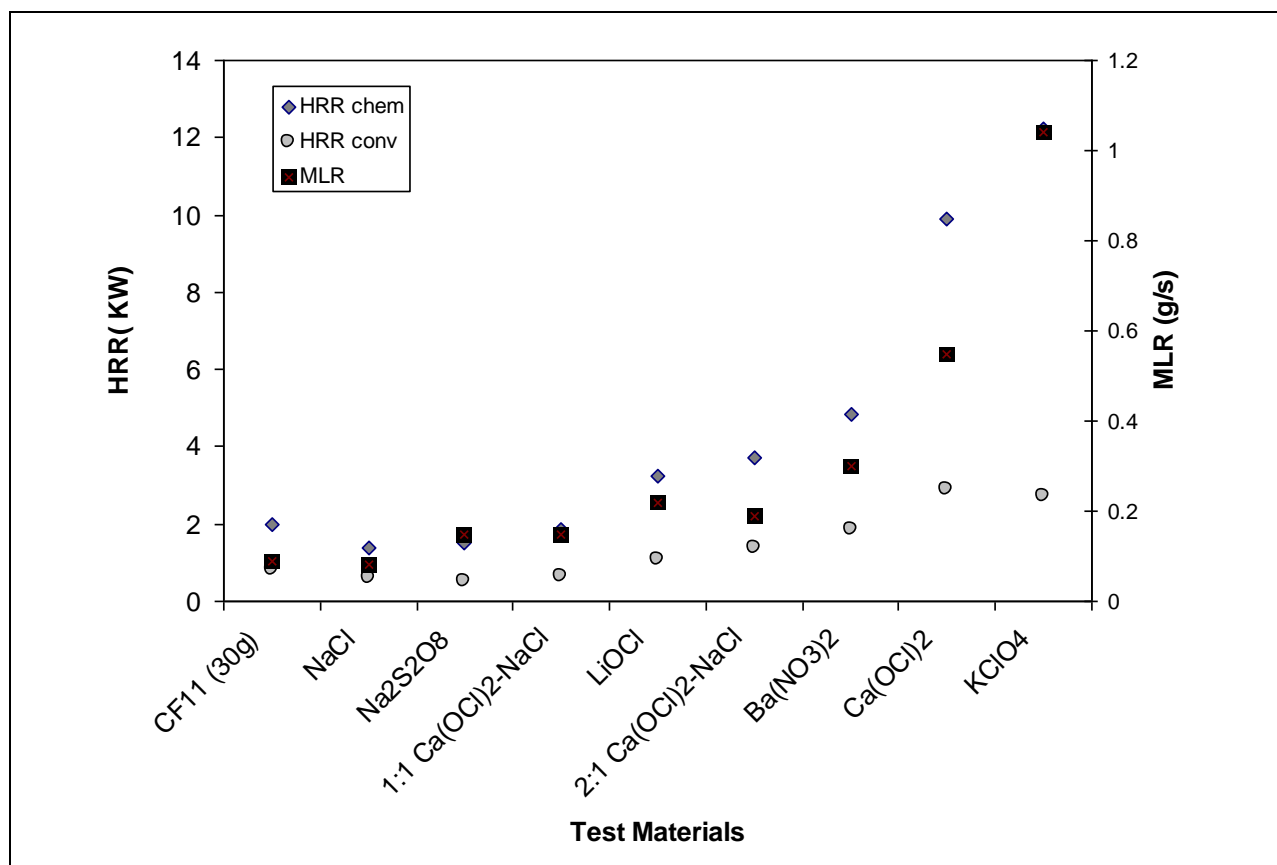
FIGURE 44. Peak heat release and mass loss rate data of 30-g cellulose powder, 1:1 sodium chloride:cellulose powder and 1:1 inorganic oxidizers with cellulose powder.

As expected, the oxidizer-cellulose powder mixtures that principally decomposed resulted in moderate mass loss rates and low heat release rates. Sodium dichlor which principally decomposed when exposed to the glowing wire at the bench scale test, for example, had intermediate mass loss rate (0.4 g/s) but low heat release rate (0.4-0.7 kW). The gaseous products released during the decomposition of 30 gram and 15 gram 1:1 trichlor:cellulose powder mixtures ignited under the forced convection conditions, which resulted in flames that extended from the pile to the opening of the exhaust collection duct and correspondingly high

convective heat release rates (2 kW from the 15 gram mixture and 4.4 kW from the 30 gram mixture). The 15 gram 4:1 trichlor:cellulose powder mixture generated significant gaseous products seconds after the wire was energized. The mass loss rate of the 15 gram 4:1 mixture (1.0 g/s) was higher than the 15 gram 1:1 mixture (0.45 g/s). A momentary ignition of the gaseous products from the 4:1 mixture occurred but was not sustained. This was reflected by the lower peak convective heat release rate (0.7 kW). The 9:1 lithium hypochlorite (29%):cellulose powder mixture phase changed from a granular solid to a slurry when exposed to the glowing wire at the bench scale; the same behavior was observed during the FPA test, and the mixture's peak heat release rate (1.5 kW) was low.

Liquid Oxidizers

The ad hoc tests with the liquid oxidizers on a glass rod exposed to a Bunsen burner resulted in a visible increase in burning at the glass rod. The flame from the sodium permanganate was yellow; the permanganate solution was dried but not consumed on the glass rod. When added to dry cellulose powder in a metal dish and exposed to a gas flame, neither the wet hydrogen peroxide nor sodium permanganate cellulose powder ignited or increased the combustion of the adjacent cellulose powder. When contained inside the bulb of a plastic pipette and the pipette ignited with a small flame, the plastic ceased to burn when it contacted the liquids. When a small flame was applied directly to the bulb containing the liquid, heat was absorbed by the liquid, and no vigorous burning was observed. When a thin film of hydrogen peroxide was added to cellulose paper, the liquid dried without spontaneous ignition. When a thin film of sodium permanganate was applied to cellulose paper, the liquid dried, gaseous products were evolved, and the contaminated paper spontaneously ignited.

Additional research is required to better define the fire scenario of liquid oxidizers. Specifically, the fire scenarios to be evaluated should distinguish between the oxidizer in its as-stored liquid phase and concentration and the liquid as a contaminant that can react with a combustible material.

DEVELOPMENT OF REACTION-TO-FIRE CRITERIA

The objective of the research project was to develop test(s) and criteria for classifying oxidizers based on the degree to which the oxidizer, either by decomposition, release of oxygen or other oxidizing gas and heat, increased or enhanced the burning rate of typical combustible fuels to be consistent with the fire codes classification of Class 1 (does not moderately increase the burning rate), Class 2 (causes a moderate increase in the burning rate), and Class 3 (causes a severe increase in the burning rate)oxidizers.

The reaction-to-fire criteria for classifying oxidizers based on burning rate only was developed after completion of all bench-scale, FPA, and intermediate-scale tests. The intermediate-scale test data of the various oxidizers in combustible test packaging were evaluated relative to empty test packaging and similarly packaged sodium chloride or common salt. Further, the burning behavior of the oxidizers exposed to fire was evaluated in context of the current subjective definitions for Class 1, Class 2, and Class 3 oxidizers. The peak convective heat release rate was consistent with the observed range in burning behavior or burning rate. The time duration over which the energy was released was characteristic of strong and weak oxidizers: strong oxidizers had higher heat release rates over a shorter period of time compared to weak oxidizers that had low heat release rates over a longer period of time. Next, the bench-scale burning behavior and test data of the same materials tested at the intermediate-scale were evaluated. The screening test mass loss rate and active burning time that would characterize clearly Class 1 oxidizer behavior and clearly Class 3 oxidizer behavior were established. Oxidizers that did not clearly meet Class 1 or Class 3 mass loss rate and burning time criteria would be assigned to Class 2 until confirmatory intermediate-scale testing is done.

The intermediate- and bench-scale test results for granular sodium chloride and 11 oxidizers are summarized in Table 15. The bench-scale test data in Table 15 corresponds to the mixture with the fastest mass loss rate (i.e., 1:1, 4:1 or 9:1 mixture). Calcium peroxide is not included in Table 15 because the oxidizer tested at the intermediate-scale contained 25wt% calcium hydroxide, while the material tested at the bench-scale contained 25wt% calcium carbonate.

TABLE 15. Intermediate- and Bench-Scale Test Results of Sodium Chloride and Oxidizers.

Test Material	Intermediate-Scale (24 lbs Net Wt.) in Test Packaging			Bench-Scale Screening Test*	
	Peak Convective HRR	Peak Radiant Heat Flux	Calculated Active Burning Time	Mass Loss Rate	Active Burning Time
	kW	kW/m^2	s	g/s	s
Sodium chloride	31	0.6	315	0.05±0.01	219±012
70:30 Calcium hypochlorite w/ magnesium sulfate heptahydrate	45	1.9	180	0.17±0.03	68±4
Sodium dichlor dihydrate (granular)	49	1.2	350	0.27±0.02	78±5
Trichloroisocyanuric acid	55	2.3	208	2.45±0.67	15±2
Formulated sodium percarbonate**	66	2.6	284	0.06±0.01	222±37
Potassium monopersulfate (45%)	86	3.2	120	0.17±0.03	48±8
Sodium percarbonate (99%)	92	5.2	95	0.55±0.04	26±1
Sodium persulfate (99%)	115	4.6	110	0.18±0.03	59±4
1:1 Calcium hypochlorite-sodium chloride	131	7.3	72	0.36±0.10	24±5
2:1 Calcium hypochlorite-sodium chloride	203	12.7	52	2.32±0.43	7±1
Potassium permanganate (>97.5%)	274	14.5	56	3.5±0.47	6±1
High strength calcium hypochlorite	414	18.8	26	8.6±1.8	5±1

*Data shown as average ± sample standard deviation. ** The material tested at the intermediate-scale contained 65wt% oxidizer; the mixture tested at the bench-scale contained 40wt% oxidizer.

The materials in Table 15 are listed in the order of increasing peak convective heat release rate. By inspection, the peak radiant heat flux generally increased and the calculated active burning time decreased with increasing peak convective heat release rate. Similarly, the mass loss rate from the screening test increased and the active burning time from the mass loss data decreased with increasing peak convective heat release rate.

Figure 45 is a graph showing the bench-scale test data of the oxidizers tested at the intermediate-scale and that exhibited a range in burning behavior. The graph does not include the dichlor and trichlor test data because these materials principally decomposed. Vertical lines in Figure 45 separate materials that exhibited clearly Class 1 behavior, clearly Class 3 behavior, and intermediate behavior. A clearly Class 1 oxidizer is an oxidizer which when mixed with dried cellulose powder was slow to ignite, did not readily or rapidly spread flaming combustion over the pile and had a peak flame height less than nine inches from the test platform. A clearly Class 3 oxidizer is an oxidizer which when mixed with dried cellulose powder ignited readily, rapidly spread flaming combustion over the pile and had peak flame heights greater than nine inches from the test platform.
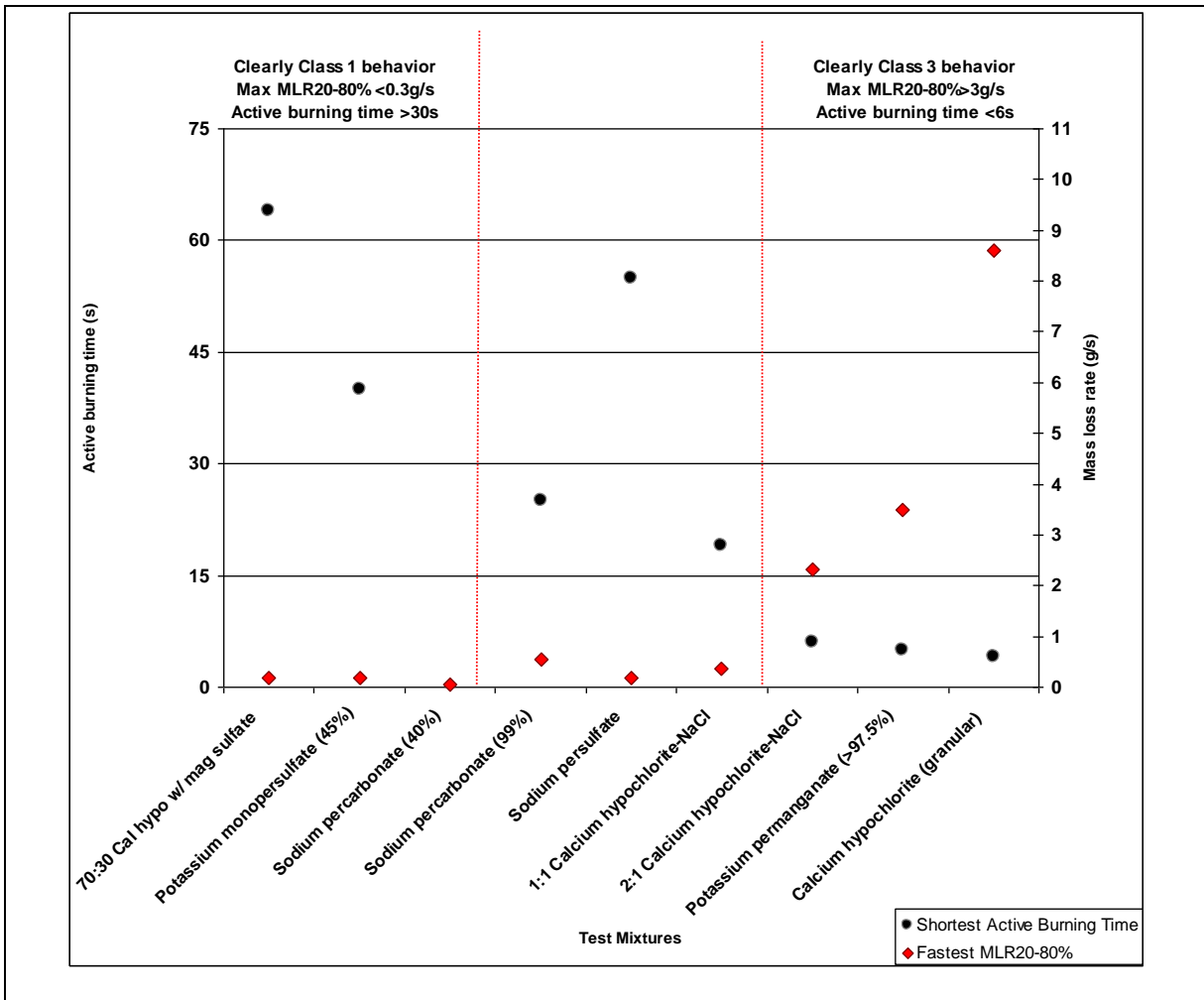
FIGURE 45. Bench-scale screening test data of inorganic oxidizers with a range in burning rate.

The inorganic oxidizers at the intermediate-scale with peak convective heat release rates greater than 200 kW had maximum mass loss rates at the bench-scale greater than 2.9 g/s and active burning times ranging from 5–7 seconds. The inorganic oxidizers at the intermediate-scale with peak convective heat release rates less than 100 kW had bench-scale mass loss rates less than 0.55 g/s and burning times longer than 26 seconds. Bearing in mind that there are many more oxidizers, the bench-scale maximum mass loss rate and active burning time for clearly Class 1 materials were rounded to 0.3 g/s and 30 seconds, respectively, and to 3 g/s and 6 seconds, respectively, for clearly Class 3 materials.

From the cumulative results of testing, one method with two reaction-to-fire tests and criteria is proposed in Table 16 and Figure 46. Using data collected from oxidizers with a range in burning behavior, burning rate was defined using fire test response characteristics namely the peak heat release rate, maximum mass loss rate and duration of active burning. The bench-scale test should be used as a first step to screen oxidizers, followed by confirmatory intermediate-scale tests for materials which are not clearly Class 1 or Class 3. Class 4 oxidizers meet the burning rate criteria of Class 3 oxidizers but require further evaluation to determine if an explosive reaction can result from reactivity and/or exposure to thermal or physical shock.

No materials tested exhibited an explosive reaction when exposed to an ignition source; although, sodium chlorate came close.

TABLE 16. Tests and Criteria for Assigning Solid Oxidizers to Class 1, Class 2, Class 3 & Class 4.

		PROPOSED TESTS AND CRITERIA			
		Bench-Scale Screening Test (30-g mixtures)		Intermediate-Scale Fire Exposure Test (24-lbs in test packaging)	
CLASS	CURRENT CRITERIA	Maximum Mass Loss Rate (MLR)* [g/s]	Active Burning Time (t_{active})** [s]	Peak Convective Heat Release Rate (HRR_{conv}) [kW]	Active Burning Time*** [s]
CLASS 1	Does not moderately increase the burning rate of combustible materials	≤0.3	≥30	≤100	≥120
CLASS 2	Causes a moderate increase in the burning rate of combustible materials	0.3<MLR<3	6< t_{active} <30	100-200	60< t_{active} <120
CLASS 3	Causes a severe increase in the burning rate of combustible materials	≥3	≤6	≥200	≤60
CLASS 4	Generally meets the Class 3 criteria plus evidence to support explosive reaction due to contamination or exposure to thermal or physical shock including UN and/or GHS designations.				

* Maximum mass loss rate from 20 to 80% the final measured mass of 1:1, 4:1 and 9:1 mixtures.

** Calculated from the mass loss profiles.

***Calculated from the width of the curve at ½ the peak radiant heat flux.

Importantly, the intermediate-scale test results were consistent with existing pallet-scale tests with Class 1 trichlor (all forms), Class 1 formulated calcium hypochlorite, and Class 3 high-strength calcium hypochlorite.[21][22]

Bench-Scale Screening Tests
with Oxidizer:Cellulose
Powder Mixtures*

Max $MLR_{20-80\%mf} \leq 0.3 g/s$
& active burning time
($t_{0-80\%mf}) \geq 30s$

Class 1 or Class 3 criteria
not met

Max $MLR_{20-80\%mf} \geq 3 g/s$
& active burning time
($t_{0-80\%mf}) \leq 6s$

Class 1

Borderline
Class 1/Class 2

Class 2

Borderline
Class 2/Class 3

Class 3

Intermediate-Scale Fire
Exposure Test with 24 lb
(10.9 kg) Oxidizer in Test
Packaging

Peak Convective $HRR \leq 100$ kW
& Active burning time $\geq 120s$

Peak Convective $HRR \geq 200$ kW
& Active burning time $\leq 60s$

Class 1

Class 2

Class 3**

100 kW< Peak Convective HRR< 200 kW
&
60s< Active burning time< 120s

* Thirty-gram (30-g) piles of 1:1, 4:1 and 9:1 by weight mixtures of the oxidizer, with the as-received particle size, and dried cellulose powder. If the 1:1 or 4:1 oxidizer: cellulose powder mixture result in burning durations less than 6 seconds or mass loss rates greater than 3 g/s, testing a 9:1 mixture is not required.

** A Class 4 oxidizer generally meets the Class 3 burning rate criteria plus evidence to support explosive reaction due to contamination or exposure to thermal or physical shock.

FIGURE 46. Flow diagram of oxidizer classification tests and criteria

ADVANTAGES AND LIMITATIONS

The advantages and limitations of the bench-scale screening test and the intermediate-scale fire exposure test are summarized in Tables 17 and 18, respectively. It should be noted that the limitations of the bench-scale screening test are addressed by the intermediate-scale fire exposure test. As a result, the proposed method with two reaction-to-fire tests is better than a single test.

TABLE 17. Advantages and Limitations of the Bench-Scale Screening Test

Advantages	Limitations
Evaluated by inter-laboratory testing	Cannot accommodate tablets
Does not require expensive equipment	Not representative of packaged oxidizers
Test operator independent data	Does not evaluate plastic as a typical combustible fuel
Capable of evaluating pure materials, formulations, mixtures and various particle size	Does not provide calorimetric data
Economical	Does not assess combustion products composition and/or toxicity
Less waste generated	

TABLE 18. Advantages and Limitations of the Intermediate-Scale Fire Exposure Test

Advantages	Limitations
More realistic than 30-g mixtures with cellulose powder	Requires test facility and trained personnel
Less expensive than pallet scale	More expensive than screening test
Can accommodate tablets	Can be damaging to equipment
Provides calorimetric data	Test packaging instead of actual packaging
Added instrumentation can include combustion gas analysis	

A reliable, bench-scale screening test was one goal of the research project. The bench-scale screening test used in these studies was an improvement on and provides more information than the current UN Test O.1 method for solid oxidizers. It provided test-operator independent data and was able to distinguish between weak oxidizers, oxidizers that decompose, and strong oxidizers. The inclusion of thermocouples above the test platform provided additional information to distinguish between combustion and decomposition.

In terms of the test set-up, the added instrumentation (i.e., laboratory balance with data output, four thermocouples, video camera) did not add significantly to the cost or complexity of the test. Once set-up, a series of tests (e.g., up to 15 trials) could be performed in one day. Fewer tests are required per oxidizer because the proposed test methodology and criteria do not require a reference oxidizer for classification. Video recordings showed the range in burning behavior, so their use are strongly recommended.

The method of collecting mass loss data during combustion of oxidizer-fuel mixtures was the subject of inter-laboratory testing and has been shown to be reproducible. Starting in February 2009, twelve laboratories participated in round-robin testing with three granular oxidizers under Solvay's leadership for the IGUS Ad hoc Working Group on the Solid Oxidizer Test (UN Test O.1). Another major finding of the inter-laboratory testing was criterion based on mass loss rate, in comparison to stop-watch burning time, was less likely to result in the assignment of an oxidizer to the wrong packing group (for transportation).

The 30-g screening test is useful to screen materials for dangerous properties. While it does not provide calorimetric data, more tests can be done at the bench scale. It can be performed by lab technicians using typical laboratory equipment; it is versatile; it can be used to examine and distinguish between pure materials and admixtures; and it provides information previously unavailable, including test-operator-independent rate data, temperature, and flame height. The limitations of mass loss are well known. Mass loss, like burning time, is not an inherent or intrinsic property of the material being tested; it does not assess the release of smoke or combustion products; and it is not always a result of combustion. Indeed, ASTM E 2102

recognizes that "for materials or products containing sorbed water or molecularly bound water, the mass loss observed will be a somewhat inaccurate representation of the combustion process as the water mass loss will overstate the process." The added temperature data from thermocouples placed above the pile resolves this issue.

Notably, oxidizers are not sold as intimate mixtures with cellulose powder and the combustible material with which the oxidizer comes into contact may be plastic and not cellulosic. Plastic fuels, either powder or pellets, were examined as a fuel in oxidizer mixtures at the bench-scale, but the end-point of combustion was obscured as pools of molten plastic continued to burn after the oxidizer was consumed. Mixtures of oxidizer with plastic fuel were also observed to expel molten plastic droplets from the test platform.

ASTM E 2102 provides guidance on the addition of a short stack and thermopile above the test material to estimate heat release rate based on gas temperatures; however, identifying and calibrating a thermopile requires additional research. On the other hand, combustion-type FPA tests measure heat release rate and, when used in combination with the material's composition, provides fundamental reaction-to-fire properties. The FPA has recently been used to characterize the heat release rate of two potassium nitrate based smoke powder mixtures and energetic materials.[23]-[24] The FPA could have potential added value when investigating material-specific properties, including formulations and reactions with inert and hydrated salts compared to the pure oxidizer without additives. The FPA could be used to investigate the influence of aged or aging stored materials such as dehydration and slow decomposition on the heat release rate of the material.

The intermediate-scale fire exposure test with 24 lbs net weight of the oxidizer in combustible test packaging meets all the criteria for a reliable, scientific, and realistic test for classifying oxidizers. The intermediate-scale fire exposure test data showed (1) can accommodate oxidizers with a range in burning behavior and (2) can distinguish the influence of oxidizer concentration and/or formulation on the quantity and duration of energy released.

Like the FPA, the intermediate-scale test provides heat release rate data. The heat release rate is most often used and considered the best parameter for characterizing the intensity of a fire and is the single most important parameter for characterizing fire hazard for storage protection. The convective heat release rate is an accepted but indirect measurement of the heat release rate based on the increase or rise in temperature of the combustion gases. It does not include the composition of the gaseous products. The chemical heat release rate is direct assessment of the combustion reaction based on the composition and volume of gaseous products collected. The convective heat release rate is typically lower than the chemical heat release rate because some of the heat during combustion is lost as radiant energy. The determination of heat release rate is applicable to small, intermediate and large scale fire tests. The criterion for classification based on peak convective heat release rate of the packaged material was chosen because it applies to all oxidizers irrespective of its composition and some oxidizers produce gaseous products that may be destructive to gas analysis instrumentation required for the chemical heat release rate determinations.

In addition to combustibility, low, moderate, or high heat release rates are used to classify occupancies and commodities in the design of sprinkler protection.[25] The heat release rate of oxidizers could be used in modeling the sprinkler discharge densities.

Although more realistic than an oxidizer intimately mixed with cellulose powder, the intermediate-scale test requires a fire test laboratory and staff. For safety reasons, intermediate-

scale testing must be proceeded by some level of bench-scale screening tests. The intermediate-scale fire exposure test is less expensive than a pallet-scale test but more expensive than a bench-scale test. It generates less waste than a pallet-scale test but more waste than a bench-scale test. A limited number of intermediate-scale tests were allowed by the project budget. Thus, it was impossible to also establish the uncertainty in the fire-test-response characteristic(s) at the 24-lb scale that covers the range in oxidizer burning behavior. An ASTM standard guide provides an assessment of the measurement uncertainty, error, precision, repeatability, and reproducibility in fire tests.[26] Future research should include collecting data from multiple fire exposure trials with salt and, at a minimum, three different oxidizers with a range in burning behavior in the same test packaging to assess the uncertainty estimates and quality of data. Inter-laboratory testing of the same oxidizer in the same test packaging would provide information on repeatability.

When combined, the bench-scale screening test reduces the cost associated with intermediate-scale fire exposure testing. Intermediate-scale testing would be required for borderline Class 2, Class 2, and borderline Class 3 oxidizers. The screening test also can be used to preliminarily classify oxidizers and/or to study the influence of admixtures, diluents, exotherm control agents, particle size and water content on burning rate. If the test material by mass loss and active burning time were not clearly Class 1 or clearly Class 3, then it would be a Class 2 oxidizer. The manufacturers can accept Class 2 assignment or proceed to intermediate-scale testing with 24 pounds of the oxidizer in the test packaging to resolve whether the oxidizer is a high Class 1 and not Class 2, Class 2, or Class 3.

While not required for classification, the intermediate-scale fire exposure test could be used to distinguish an influence of product form and packaging on burning rate. In general, packaging can add combustible material for reaction with the oxidizer and can influence the time for fire to penetrate the packaging and the rate of fire spread through the packaging. Eventually, the quantity of fuel from packaging will influence the heat release rate. In this project, three materials were tested in both granular and tablet form. The tablet form materials had lower peak convective heat release rates, but it did not change the burning behavior from that of the expected Class.

The proposed tests and criteria do not require a reference oxidizer for classification. Fire hazard assessment procedures recognize the use of inert materials for comparing the ignition propensity and heat release rate with the class of materials under investigation.[27] For the determination of the degree of enhanced burning rate, the use of an inert material is more meaningful than the use of a reference oxidizer. Potassium bromate (the reference oxidizer in UN Test O.1) contains and releases oxygen as the oxidant. Other oxidizers may not contain the same amount of oxygen in their chemical structure to release during combustion and/or may release oxidants other than and/or in addition to oxygen (i.e., nitrates, persulfates) or have different decomposition temperatures or combustion reactions. Potassium bromate is also toxic. Sodium chloride (NaCl) does not decompose or undergo a phase change when exposed to a glowing wire or the propane burner temperatures and is available in both granular and tablet forms.

Each oxidizer and/or formulated product must be evaluated. There should be no substitution of one oxidizer with other similar oxidizers. For example, the burning rate of calcium peroxide is very different than sodium peroxide. Neither reaction-to-fire test provides information on thermal stability, reactivity, nor the toxicity of the gaseous products generated. Thermal decomposition studies and reactivity tests were outside the scope of the current project. Standard fire test methods for evaluating the toxicity of decomposition and/or combustion products include ASTM

E 800[28] and NordTest Method NT Fire 047[29] and/or time-resolved gas analysis coupled with fire test instruments that provide calorimetric data. Other analytical techniques and instrumentation (i.e., impingers) are required for detecting symmetric molecules such as chlorine. Similarly, mass balance and the chemical analysis of the oxidizer and/or oxidizer-fuel mixture before and after combustion-type tests can be used to provide some information regarding the gaseous products released during combustion and/or decomposition. For corrosion studies, painted and bare metal coupons with a known initial mass can be suspended in and exposed to the gaseous decomposition and combustion product stream. The corrosion rate can be monitored by changes in surface morphology and mass loss over time.

Comparison to Current Oxidizer Class Assignment

The current Class assignment of oxidizers used in this research project was not used in the development of the criteria. Using test data and the proposed criteria, some tested oxidizers had Class assignments different from their current Class. The oxidizers tested and their Class assignment based on the screening test and intermediate-scale tests are summarized in Table 19. The oxidizers for which there was only screening test data are summarized in Table 20.

TABLE 19. Combined Results and Class Assignments of Oxidizer

Oxidizer (Concentration)	Screening Test (30 g Mixtures)* Max MLR 20-80%wt (g/s)	Active Burn Time 0-80%wt (s)	Class	Intermediate Scale Fire Exposure in Test Packaging Test Pkg.**	Mass Pkg. & Oxidizer (lbs)	Peak HRRconv (kW)	Active Burn Time (s)	Class	Current Class****
Trichlor (99% w/ 90%Avail Cl₃) Granular	2.45	15	2	Carton 1	26.7	55	208	1	1
Trichlor - 3" Tablets	-	-	-	Carton 1	26.7	38	230	1	1
Trichlor - 1" Tablets	-	-	-	Carton 1	27.0	39	320	1	1
Sodium Dichlor Dihydrate (99%)	0.27	78	1	Pail	26.1	39	584	1	1
70-30 Cal Hypo-Mag Sulfate (50.87%Avail Cl₂, 22%H₂O) ***	0.17	68	1	Carton 1	25.9	45	350	1	1
Formulated Potassium Monopersulfate (<45% KHSO₅ or <90% 2KHSO₅·KHSO₄·K₂SO₄)	-	-	-	Carton 1	26.7	58	180	1	Not Listed
Potassium Monopersulfate (45% KHSO₅ or ~90% 2KHSO₅·KHSO₄·K₂SO₄)	0.17	48	1	Carton 1	26.7	86	120	1	Not Listed
Sodium Percarbonate (65%)	-	-	-	Carton 1	26.3	66	234	1	1
Sodium Percarbonate (99%)	0.55	26	2	Carton 1	26.7	92	95	1 or 2	1
Sodium Persulfate (99%)	0.18	59	1	Carton 1	26.9	115	110	2	1
Calcium Peroxide (75%) w/ calcium carbonate	4.35	8	2 or 3	-	-	-	-		1
Calcium Peroxide (75%) w/ calcium hydroxide	-	-	-	Carton 1	26.3	127	116	2	2
1:1 Cal Hypo – Sodium Chloride (33% available chlorine)	0.36	24	2	Carton 1	26.1	131	72	2	2
				Pail	25.4	149	80	2	
				Carton 2	25.7	164	30	2 or 3	
2:1 Cal Hypo – Sodium Chloride (48% available chlorine)	2.32	7	2	Carton 1	26.1	203	52	3	2
				Carton 2	25.7	303	22	3	
Potassium Permanganate (>97.5%)	3.5	6	3	Carton 1	26.8	274	56	3	3
Cal Hypo - Briquettes	-	-	-	Carton 1	26.5	403	36	3	3
Cal Hypo - Granular	13.8	6	3	Carton 1	25.1	414	26	3	3
					14.1	194	26		
Potassium Perchlorate (99%)	9.59	6	3	Carton 1	14.8	152	50	3	2
					14.8	195	34		

* Data shown are average values over multiple trials of each mixture with the highest mass loss rate. ** Carton 1– 6 HDPE containers in DW carton; Carton 2– 24 1-lb bags in DW carton; Pail – 2.5 gallon HDPE pail with lid. - = not tested at bench scale; *** The formulated 70:30 calcium hypochlorite:magnesium sulfate heptahydrate is an intentional blend of high strength (73%) calcium hypochlorite (5.6% water) and an additional diluent, magnesium sulfate heptahydrate (51wt% water); the calculated percent available chlorine and moisture content of the admixture are reported in the Table. ****From NFPA 430 (2004) Annex B or NFPA 400 (2009) Annex G.

Table 19 lists 14 different oxidizers; formulations are considered or counted as 'different' but the same material in the same concentration and/or granular and tablet form are counted as one material. The gray shaded cells indicate instances where the assigned class differed from the current NFPA Class. Included with the 14 oxidizers are potassium monopersulfate triple salt and a formulated potassium monopersulfate commercial product, both of which are not listed in the Code's Annex. The triple salt is identified as corrosive solid for transportation, most likely due to the precedence of hazards. There are no oxidizer hazard rating symbols or labels, but the MSDS and product information state that it releases oxygen.

At the intermediate-scale and exposed to fire, the granular potassium monopersulfate triple salt increased the burning rate of its combustible packaging; however, their peak convective heat release rates were well below 100 kW. The peak convective heat release rate of the diluted potassium monopersulfate containing commercial product was 32% lower than the concentrated triple salt. Both materials exhibited oxidizer-type Class 1 burning behavior.

Using the intermediate-scale test data and criteria for the remaining 12 oxidizers that are listed in the Annex, seven had burning behaviors consistent with the results of the proposed criteria. They were Class 1 trichlor (all forms), dichlor, formulated calcium hypochlorite, concentrated sodium percarbonate (99%), and diluted sodium percarbonate (65%); Class 2 calcium hypochlorite with 33% available chlorine; and, all forms of Class 3 calcium hypochlorite (>50wt%). Five of the oxidizers had burning behaviors different from their current Class. In each case, the actual burning behavior was consistent with a higher Class. In other words, they were *more hazardous* than their current Class suggests. These were sodium persulfate, calcium peroxide, potassium permanganate, potassium perchlorate, and calcium hypochlorite with 48% available chlorine. Two tests with 50 wt% calcium hypochlorite (e.g., 48% available chlorine) had peak convective heat release rates greater than 200 kW. The burning behavior was considered borderline Class 3 "severe increase in burning rate".

In order for the screening test to be meaningful, a majority of the bench-scale predictions should agree with the Class from the intermediate-scale test data. Eight of the twelve materials with bench-scale test data in Table 19 predicted the same Class as the intermediate-scale; two predicted higher; and two predicted lower than the intermediate-scale. The two oxidizers that the screening test did not assign as clearly Class 1 were trichlor, which decomposed, and sodium percarbonate, which turned out to have Class 1 behavior anyway. The intermediate-scale results for both were consistent with their current Class. These results show the screening test is conservative. In two cases, the bench-scale test data and criteria predicted Class behavior different than the intermediate-scale results. Class 1 sodium persulfate exhibited clearly Class 1 behavior at the bench-scale but had a peak convective heat release rate greater than 100-kW (Class 2) at the intermediate-scale. The 50 wt% calcium hypochlorite burned more vigorously at the intermediate-scale (Class 3) than at the bench-scale screening test (Class 2) predicted.

Eight oxidizers were only tested at the bench-scale. All the oxidizers are listed in the Code's Annex: five are current Class 1, and three are current Class 3. Barium nitrate and sodium nitrate are not specifically listed and therefore are Class 1. The Predicted Class and Current Class are compared in Table 20. Based on the bench-scale screening test results, one oxidizer was clearly Class 1, and three oxidizers were clearly Class 3. Of the remainder, intermediate-scale fire exposure testing is recommended to confirm the Class. However, the mass loss rate of lithium hypochlorite (29%) and barium nitrate shown in Table 20 were very close to the Class 1 cut-off, and 24 pounds of the material in the combustible test packaging would most likely have peak convective heat release rates less than or close to 100 kW. On the

other hand, the sodium perborate monohydrate and sodium nitrate did not exhibit clearly Class 1 behavior and the mass loss rates are not near the Class 1 cut-off. In these cases, intermediate-scale testing would be needed to determine if they are Class 1 or Class 2.

TABLE 20. Assessment of Bench Scale Screening Test Data

Oxidizer (Concentration)	Screening Test (30 g Mixtures)*			Current Class**
	Max MLR $_{20-80\%mf}$ (g/s)	Active Burn Time $_{0-80\%mf}$ (s)	Class	
Magnesium Peroxide Complex (24 to 28% MgO$_2$)	0.09	227	1	1
Lithium Hypochlorite (29wt% w/ 35% available chlorine)	0.32	33	1 $_{(Burn\ Time)}$ or 2 $_{(MLR)}$	1
Barium Nitrate (99%)	0.33	34	1 $_{(Burn\ Time)}$ or 2 $_{(MLR)}$	1 (*Inorganic nitrate*)
Sodium Perborate Monohydrate (>96%)	0.83	17	2 $_{(MLR,\ Burn\ Time)}$	1
Sodium Nitrate (>97%)	1.29	18	2 $_{(MLR,\ Burn\ Time)}$	1 (*Inorganic nitrate*)
Calcium Hypochlorite (78.6% w/ 11%H$_2$O)	4.72	6	3 $_{(MLR,\ Burn\ Time)}$	3
Calcium Hypochlorite (72.68% w/ 5.7%H$_2$O)	13.8	3	3 $_{(MLR,\ Burn\ Time)}$	3
Sodium Chlorate (99%)	17.3	3	3 $_{(MLR,\ Burn\ Time)}$	3

* Data shown are average values over multiple trials of each mixture with the highest mass loss rate.
** From NFPA 430 (2004) Annex B or NFPA 400 (2009) Annex G.

CONCLUSIONS

Burning rate is the principle physical hazard of oxidizers. The degree to which an oxidizer increases the burning rate of combustible materials with which it comes into contact is the basis of the current NFPA Classes. However, burning rate is not defined in the NFPA Code. Existing test methods for assessing oxidizers use visual burning time (i.e., seconds) or combustion propagation rate (i.e., cm/s or in/s) to characterize the enhancement or acceleration of burning rate by oxidizers in small quantities and always in comparison to a reference oxidizer. In this project, the enhancement or acceleration of burning rate by oxidizers, intentionally mixed with cellulose powder or in combustible test packaging, was evaluated in terms of fire-test-response characteristics.

In investigations of a material's response to fire, it is recognized that several judiciously designed and selected tests can provide useful indicators of relative fire hazard and materials ranking. The combined bench-scale screening test and intermediate-scale fire exposure test described herein provide a scientific method for assigning a solid oxidizer to a Class for storage. According to the National Materials Advisory Board, "the fire safety of our environment can be improved and losses from unwanted fires can be reduced significantly only as progress is made in identifying test methods which are practical, meaningful and useful in the development of safer materials, systems and designs".[30] The proposed bench-scale screening and intermediate-scale fire exposure tests are likely to improve the fire code for the storage of solid oxidizers.

RECOMMENDATIONS

The Phase II project delivers a method with two reaction-to-fire tests and criteria for assigning solid oxidizers to Class 1, Class 2, Class 3 and Class 4. Based on this research project, the following recommendations are proposed to the Hazardous Chemicals technical committee:

(1)   Adopt the proposed method with two reaction-to-fire tests and criteria for assigning solid oxidizers to Class 1, Class 2, Class 3, or Class 4.

(2)   Evaluate and refine the definitions of oxidizer, burning rate and the definitions of Class 1, Class 2, Class 3, and Class 4 oxidizers based on this report and the proposed tests and criteria.

(3)   Add a summary of this research in the Code's Annex.

(4)   Evaluate the test data and Class of oxidizers that, based on the intermediate-scale test results, differed from their current NFPA Class. These oxidizers are sodium persulfate, calcium peroxide, potassium permanganate, potassium perchlorate and calcium hypochlorite (50wt%). Under the proposed tests and criteria, each would be one class higher. Further, potassium monopersulfate should be considered for addition to Class 1 in the Code's annex.

(5)   Evaluate the burning rate of ammonium nitrate.

(6)   Establish a technical basis for the existing fire protection provisions with additional testing using Class 1-borderline Class 2 and Class 2-borderline Class 3 oxidizers.

(7)   Modify the Code to provide the same security measures recommended by the NRCan Explosive Act for specific solid and liquid oxidizers identified as explosive precursors. The oxidizers include hydrogen peroxide (≥30%), potassium chlorate, potassium perchlorate, sodium chlorate, nitric acid (≥68%), potassium nitrate, and sodium nitrate.

Additional Research

The screening test, the collection of and reducing mass loss data, has been subject to inter-laboratory testing. The following topics were identified as areas requiring additional research.

(1)   Factors influencing burning rate at the intermediate-scale including product form and packaging.

(2)   Fundamental research on oxidizers that decompose rapidly with and without flaming combustion to include an evaluation of the toxicity, corrosivity, and combustibility of the gaseous products of decomposition.

(2)   Fundamental research on the fire scenario(s) and fire hazard(s) of liquid oxidizers. Specifically, the fire scenarios to be evaluated should distinguish between the oxidizer in its as-stored liquid phase and concentration and the liquid as a contaminant that can react with and/or cause spontaneous ignition of a combustible material.

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