NATIONAL OXIDIZING POOL CHEMICALS STORAGE FIRE TEST PROJECT

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FIRERESEARCH

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FOREWORD

The National Oxidizing Pool Chemicals Storage Fire Test Project was initiated in 1996 with the aim of better understanding the burning behavior and ability of automatic fire sprinkler systems to control fires involving containerized dry oxidizing pool chemicals. This information was needed for bulk retail buildings - also known as "big box" stores - where oxidizing pool chemicals are stored in rack storage arrays.

Additionally, the data developed from the testing is for consideration by the Technical Committee responsible for NFPA 430, *Storage of Liquid and Solid Oxidizers*, and for others concerned for fire safety in large volume retail stores.

The Research Foundation expresses its gratitude to project technical director David Nugent, P.E., and fellow authors David Sheppard, P.E., and Daniel Steppan for the thorough preparation of this report, and to Underwriters Laboratories Inc. for its professional conduct of the fire tests. The Foundation also thanks the project's Technical Advisory Committee listed on the following page for its contributions of expertise and the financial resources required to complete the project.

Of course, participation does not necessarily constitute a participant's endorsement of every statement in this report.

NATIONAL OXIDIZING POOL CHEMICALS STORAGE FIRE TEST PROJECT

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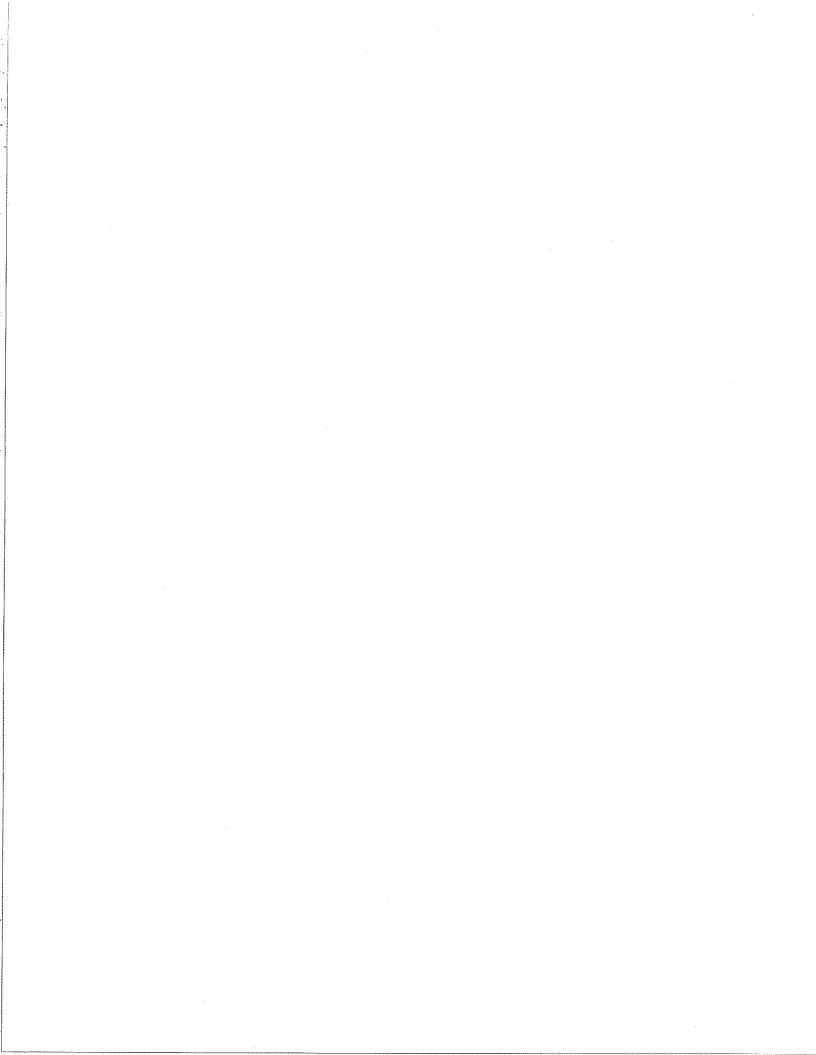
Schirmer Engineering Corporation

TEST FACILITY

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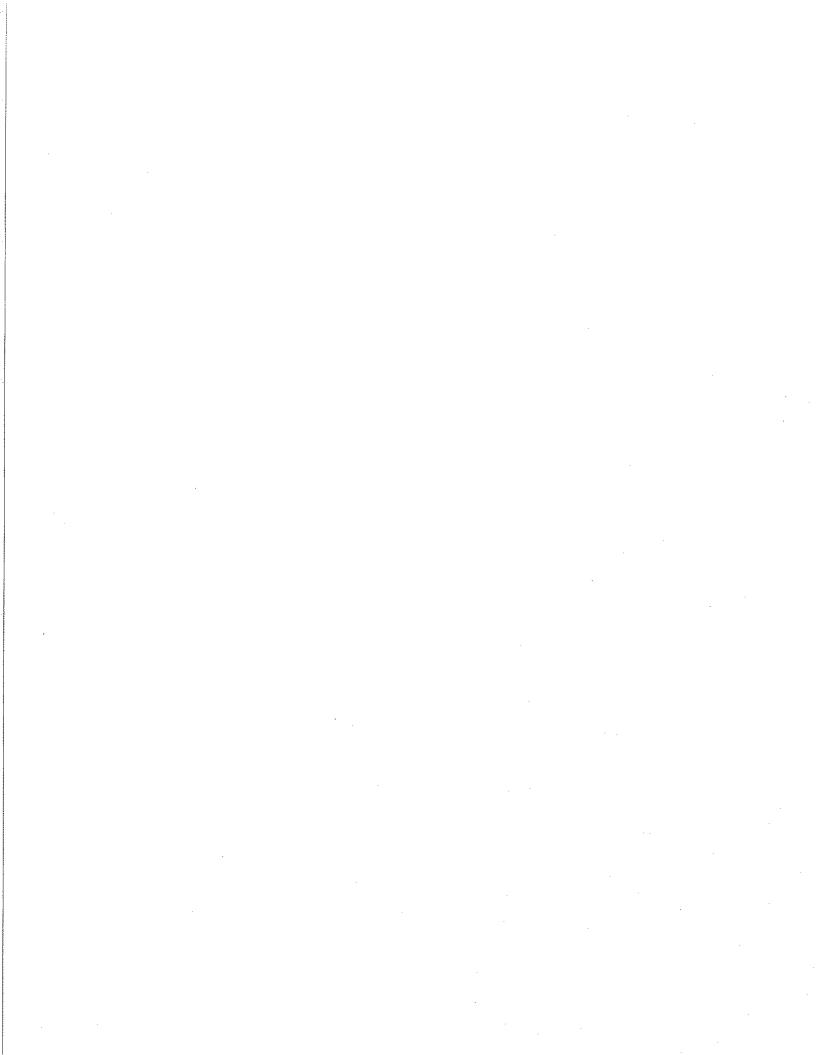
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I. BACKGROUND INFORMATION

This project was initiated out of a need to better understand the burning behavior and ability of automatic sprinkler systems to control fires involving containerized oxidizing pool chemicals. More specifically, this information was needed for bulk merchandizing retail buildings, also known as *big box* retailers, where oxidizing pool chemicals are stored in rack storage arrays.

Underscoring the need for this information is the fire loss history associated with oxidizing pool chemicals. Over the past few years there have been some highly publicized fires at large volume retail stores where oxidizing pool chemicals were involved.

Additionally, NFPA 430, "Code for the Storage of Liquid and Solid Oxidizers", has developed in an environment where data on burning behavior and sprinkler system performance was absent.

The current NFPA 430 oxidizer classification system "is based on the Technical Committee's evaluation of available scientific and technical data, actual experience, and its considered opinion" (Section 1-6). The fire and reactivity behavior of liquid and solid oxidizers is the basis for this classification system. This behavior includes an oxidizer's ability to increase the burning rate or cause spontaneous ignition of a combustible material. Also, the reactivity behavior of oxidizers includes those that can undergo a self-sustained decomposition or an explosive reaction.

The oxidizer categories are currently defined in NFPA 430 as follows:

Class 1 - An oxidizer whose primary hazard is that it slightly increases the burning rate but does not cause spontaneous ignition when it comes in contact with combustible materials.

Class 2 - An oxidizer that will cause a moderate increase in the burning rate or that causes spontaneous ignition of combustible materials with which it comes in contact.

Class 3 - An oxidizer that will cause a severe increase in the burning rate of combustible materials with which it comes in contact or that will undergo vigorous self-sustained decomposition due to contamination or exposure to heat.

Class 4 - A oxidizer that can undergo an explosive reaction due to contamination or exposure to thermal or physical shock. In addition, the oxidizer will enhance the burning rate and can cause spontaneous ignition of combustibles.

This classification system is not based upon quantified data, is subject to interpretation, and therefore remains subjective.

The sprinkler system design criteria listed in the current NFPA 430 is based on engineering judgment and not based upon actual sprinklered fire test data nor does it cover the available range of display and storage options. A limited number of proprietary fire tests were conducted in the 1970's. The documentation from those tests is not publicly available. However, based upon these qualitative fire tests, Section 2-11.2 of NFPA 430 contains a note that states "For certain oxidizers in combustible containers, (e.g., calcium hypochlorite in plastic containers) automatic sprinkler protection is effective only for the control of exposure fires."

The Technical Advisory Committee for this project elected to focus on trichloroisocyanuric acid (available chlorine 89%) and calcium hypochlorite (available chlorine \geq 68%), currently classified in NFPA 430 as Class 1 and Class 3 oxidizers respectively.

The increasing availability of such products, and the desire of consumers, retailers, and manufacturers to have them safely marketed in economical quantities is now driving the need to improve the fire protection measures that now exist in NFPA 430.

II. PROJECT OBJECTIVES

The objective of this project was to develop documentation for storage parameters and automatic sprinkler protection design criteria for controlling fires involving trichloroisocyanuric acid and calcium hypochlorite stored in bulk merchandizing retail buildings. The data produced as a result of this project should be capable of supporting changes in NFPA 430 regarding storage parameters and automatic sprinkler protection design criteria. These changes should allow operators of large volume retail stores to safely store these commodities to higher storage heights than currently allowed by NFPA 430.

III. PROJECT TASKS

A. Overview

This project was divided into three tasks as follows:

- Literature search and abstracts
- Large-scale calorimetry fire tests
- Sprinklered fire tests

A search of the literature was conducted to determine if information existed on the burning behavior of containerized trichloroisocyanuric acid and calcium hypochlorite. This search also included a review of the literature for information on the performance of automatic sprinkler systems with trichloroisocyanuric acid and calcium hypochlorite.

The search revealed that this information was not available. However, a number of publications were found that have information covering properties, reactivity, fire hazards and loss information. These publications have been listed and are abstracted.

Fire tests were also performed under a large scale calorimeter to obtain comparative data for empty containers and cartons, pea gravel filled containers and cartons, containerized trichloroisocyanuric acid, and containerized calcium hypochlorite. The empty and pea gravel filled containers are considered "ordinary commodities."

The purpose of these tests was to determine if either trichloroisocyanuric acid or calcium hypochlorite affected the burning rate of the "ordinary commodities" when involved in a fire. This effort was intended to better categorize these commodities per the classification system in NFPA 430. Also, these tests were also used as a screening tool to determine which commodity would be subject to sprinklered fire tests.

It was agreed that if one or both of these commodities did not increase the burning rate of the "ordinary commodities", they would not be subject to sprinklered fire tests.

The sprinklered fire tests were performed to develop documentation for storage parameters and automatic sprinkler protection design criteria for oxidizing pool chemicals that are stored in bulk merchandizing retail buildings.

B. Literature Search and Abstracts

A review of the literature revealed that there was no data in the public domain supporting or expanding on the NFPA 430 classification system or the storage/sprinkler system design criteria. Some information was available on calcium hypochlorite regarding thermal stability and sensitivity to contamination, thermochemistry of the decomposition process, loss history, and general safety issues.

The literature research information is reflective of materials sold today, however a number of improvements and changes in the process and raw materials have likewise made the materials different in many ways.

Some of the information in the abstracts that have been cited is anecdotal. All oxidizing agents will react with organic materials such as oil, grease, gasoline, lighter fluids, hydraulic fluids and liquid algaecides along with other liquid materials. These reactions may produce enough energy to ignite paper, cardboard or other combustible materials.

The cal hypo products produced today are manufactured with higher purity raw materials than in the past. This is accomplished to reduce the probability of contaminates. They are also produced with a much higher water content (usually 5.5 - 8% moisture) than in the past. The anhydrous materials (70% calcium hypocholorite)

referred to in the abstracts were produced with less than 2% moisture and would react very differently than products manufactured now.

Olin Chemical reports that a 75%+ cal hypo product on the market which is manufactured by a new patented process containing 5.5 - 8% moisture reacts no differently than the standard 65% available products.

A total of 17 relevant publications have been abstracted and may be found in Appendix G.

C. Large-Scale Calorimetry Fire Tests

1. Samples

The samples used in this investigation consisted of commodity packed in plastic bottles. The plastic bottles were enclosed in corrugated cartons. The commodities in the cartons were stacked onto two hardwood pallets. A description of the test samples is provided in Table 1.

Table 1. Sample Descriptions

Free- burn test	Commodity	Packaging	Cartons Used in Test
1	Trichloro-s-Triazinetrione (granular)	18 two pound plastic bottles in corrugated cartons. The corrugated cartons were 10" x 10" x 19_".	40
2	Calcium Hypochlorite (granular)	24 one pound plastic bags in corrugated cartons. The corrugated cartons were 12_" x 12_" x 10".	48
3	Calcium Hypochlorite (granular)	30 one pound plastic bottles in corrugated cartons. The corrugated cartons were 11_" x 13 _" x 13".	36
4	Pea Gravel	18 two pound plastic bottles in corrugated cartons. The corrugated cartons were 10" x 10" x 19_".	40
5	Empty Containers	18 two pound plastic bottles in corrugated cartons. The corrugated cartons were 10" x 10" x 19_".	40
6	Trichloro-s-Triazinetrione (Tablets, 1" diameter by 5/8" thick)	18 two pound plastic bottles in corrugated cartons. The corrugated cartons were 10" x 10" x 19_".	40

The plastic containers used in tests 1,4,5, and 6 had a volume of approximately 1100 ml.

The weights of the commodities on the pallets are listed in Table 2.

Free-burn test	Pallet 1	Pallet 1 w/ Commodity	Pallet 2	Pallet 2 w/ Commodity	Total Weight
1	52.0	882	58.9	898	1891
2	46.9	684	44.8	692	1468
3	55.7	690	36.3	670	1452
4	57.3	774	50.1	750	1631
5	42.1	108	42.1	108	300
6	56.5	888	55.2	882	1882

Table 2. Sample Weights (lbs)

Figure 1 shows a schematic of the samples stacked on a pallet. The hardwood pallets used in this test series had nominal dimensions of 48 by 40 by 5 inches. The dimensions of the samples tested are provided in Table 3.

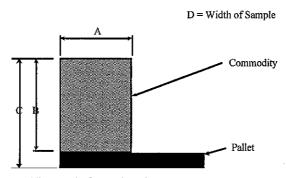


Figure 1. Sample Dimensions

		<u>'</u>		
Free-burn test	Α	В	С	D
1	20	38 _	43 _	50 _
2	25 _	30	34	50
3	23	38	43 _	41
4	20	38 _	43 _	50 _
5	20	38 _	43	50
6	20	38	43	50

Table 3. Sample Dimensions

The samples were neither prepared under witness of nor selected by an Underwriters Laboratories' representative. Identification tests to verify the components used were not conducted.

2. Facility & Equipment

The tests were conducted at UL's large scale fire test facility located in Northbrook, IL. The tests were conducted in a test cell having nominal dimensions of 50 by 50 by 65 ft

high. This test cell is fitted with a heat release calorimeter having a 25 ft diameter smoke collector and exhaust system having a nominal 10 MW capacity. The calorimeter was equipped with oxygen consumption calorimetry and convective heat release rate equipment.

3. Data Collection

All transducer and gas species data was collected using an electronic data acquisition system with a scan rate of 2 seconds.

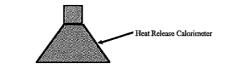
Two VHS video cameras were used to record each test.

Ignition Source

Two igniters were used in each test. The igniters were constructed from a 3 inch diameter 3 inch long cellulosic bundle soaked with 4 fluid ounces of gasoline and wrapped in a polyethylene bag. The igniters were placed in the center of the flue space.

Test Procedure

The test procedure consisted of placing two half pallets of the commodity under the calorimeter with a 6 inch flue space between the pallets. Two cellulosic igniters were placed between the pallets. The igniters were ignited with a propane torch to initiate each test. The tests were terminated when all signs of flaming combustion ceased.



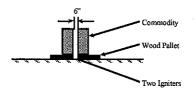


Figure 2. Test Set-Up

6. Results

The convective and total chemical heat release rate results were analyzed to determine the peak and average values these results are provided in Table 4 and Table 5.

Table 4. Convective Heat Release Rate Results [1]

Free- burn test	Sample	Peak (kVV)	Peak One Minute Average (kW)	Peak Five Minute Average (kW)	Peak Ten Minute Average (kW)
1	Trichloro-s- Triazinetrione	649	554	[4]	[4]
2	Calcium Hypochlorite	6696	4515	1705	1050
3	Calcium Hypochlorite	16184 [2]	10650 [2]	4981 [2]	3019 [2]
4	Pea Gravel	464	420	[4]	[4]
5	Empty Plastic Containers in Corrugated Cartons	1736	1458	1212	1068
6	Trichloro-s- Triazinetrione	877	767	627	457

Table 5. Total Chemical Heat Release Rate Results [1]

Free- burn test	Sample	Peak (kW)	Peak One Minute Average (kW)	Peak Five Minute Average (kW)	Peak Ten Minute Average (kW)
1	Trichloro-s- Triazinetrione	981	733	[4]	[4]
2	Calcium Hypochlorite	[3]	[3]	[3]	[3]
3	Calcium Hypochlorite	[3]	[3]	[3]	[3]
4	Pea Gravel	1210	1057	[4]	[4]
5	Empty Plastic Containers in Corrugated Cartons	3546	3054	2437	1994
6	Trichloro-s- Triazinetrione	1866	1596	1168	787

- Note 1. The heat release calorimeter has been calibrated up to 10,000 kW.
- Note 2. The values listed are less than the actual values because of spillover of the combustion products from the smoke collector.
- Note 3. Oxygen consumption calorimetry could not be used to determine total chemical heat release rate because calcium hypochlorite produces oxygen as it burns.
- Note 4. Less than the minimum resolution of the calorimeter.

Graphs of convective heat release rate and oxygen concentrations are provided in Appendix A and B respectively.

Photos of large-scale calorimetry tests appear in Appendix E.

D. Sprinklered Fire Tests

1. Samples

General

Two commodity types were used in this investigation:

Designation*	Chemical	Packaging
70 Lb. Bucket	Dry Chlorinator Calcium Hypochlorite 68%, 32% inert ingredients	Plastic Bucket. 20 inches high, 12.25 inch bottom diameter, 14.5 inch top diameter.
30 X 1 Lb. Box	Calcium Hypochlorite 78%, 22% inert ingredients	Corrugated cardboard (single flute design) containing 30, one pound plastic bottles.
		The cartons were 11.25 X 13.5 X 13.25 inches high. The cartons were constructed of an outer layer consisting of four sides and a top, and an inner display carton consisting of a bottom with three full height sides and a 2.5 inch high front. The front was double thickness.
		The thirty bottles were stored on two levels with one piece of corrugation between. The corrugation sheet was bent up for 2 inches on each side. The bottles were 2.75 X 3.5 X 6 inches high.

In the report, these samples have been referred to by their designations.

2. Test Set-up

Tests 1 through 4 were conducted on "open deck" hardwood pallets nominally 42 in. by 42 in. by 5 in. high. The pallets had wood slats which provided an air gap at the bottom of the commodity. Tests 5-12 were conducted with a 42 in. by 42 in. by nominal 1/2 in. thick piece of plywood covering the entire top of each hardwood pallet. This is designated as a "closed deck" pallet in this report.

An array of empty standard Group A plastic outer cardboard boxes were set up across an 8 ft. aisle to investigate radiation effects on a target array. These targets were not used in tests where commodity was loaded in the upper tier.

Sprinkler Test 1 - Four, 70 Lb. plastic buckets of calcium hypochlorite were assembled on two open deck wooden pallets in the lower tier of the test enclosure. The buckets were arranged two high, each group of two on a separate pallet (see Appendix F, Photo 2). The pallets were separated to provide a 6 in. nominal flue. The buckets were positioned on the pallet with a 3 in. offset to the edge defining the flue.

<u>IGNITION</u>: Two half standard ignitors were placed at the base of each of the two stacks.

<u>Sprinkler Test 2</u> - Repeat of Sprinkler Test 1. This test was repeated because Sprinkler Test 1 was inadvertantly terminated early.

Sprinkler Test 3 - Four, 30 X 1 Lb. bottles of calcium hypochlorite product in cardboard boxes were assembled on two open deck wooden pallets in the lower tier of the test enclosure. The boxes were arranged two high with two additional empty cardboard boxes on top. Each group of four boxes were placed on a separate pallet (Appendix F, Photo 3). The pallets were separated to provide a 6 in. nominal flue. The boxes were positioned on the pallet with a 3 in. offset to the edge defining the flue.

<u>IGNITION</u>: Two half standard ignitors were placed at the base of each of the two stacks.

Sprinkler Test 4 - Twelve, 70 Lb. plastic buckets of calcium hypochlorite were assembled on two open deck wooden pallets in the lower tier of the test enclosure. The buckets were arranged two high, three wide as shown Appendix F, Photo 4, with each group of six on a separate pallet. The pallets were separated to provide a 6 in. nominal flue.

<u>IGNITION</u>: Two half standard ignitors were placed at the base of the outer two stacks of buckets on the open deck wood pallet.

<u>Sprinkler Test 5</u> - Ten, 70 Lb. plastic buckets of Calcium Hypochlorite were assembled on two closed deck wooden pallets in the lower tier of the test enclosure. The buckets were arranged with the central "stack" one high and the outer two stacks two high to provide three stacks wide as shown in Appendix F, Photo 5. Each group of five was on a separate pallet. The pallets were separated to provide a 6 in. nominal flue.

IGNITION: Two half standard ignitors were placed at the base of the outer two stacks of buckets on the closed deck wooden pallet.

Sprinkler Test 6 - Ten, 30 X 1 Lb. bottles of calcium hypochlorite product in cardboard boxes were assembled on two closed deck wooden pallets in the lower tier of the test enclosure. The boxes were arranged with the central "stack" three high and the outer two stacks one high to provide an inverted "tee" arrangement as Appendix F, Photo 6. Each group of five was on a separate pallet. The pallets were separated to provide a 6 in. nominal flue with the boxes positioned flush with the pallet's edge defining the flue.

<u>IGNITION</u>: Two half standard ignitors were placed at the base of the central stacks of cardboard boxes on fire bricks.

<u>Sprinkler Test 7</u> - Same arrangement as Sprinkler Test 6 except the pressure was reduced to 25 psig.

Sprinkler Test 8 - Four, 30 X 1 Lb. bottles of calcium hypochlorite product, two open "hand pick" arrangement and two in cardboard boxes were assembled on the lower level of the upper tier. Four additional empty cardboard boxes were arranged on the outside to provide an overall four wide by two deep arrangement on this lower level

(Four full boxes total on this level). Solid plywood shelving was used to support the lower shelf (and ceiling for tests 1-7). Additionally, eight cardboard boxes (no "hand pick") were arranged on an upper level supported by a wire mesh shelf. Two of these upper eight boxes contained the calcium hypochlorite product, six were empty. The two full boxes were centered on the front of the array. See Appendix F. Photo 7.

IGNITION: A single half standard ignitor was placed in the lower shelf, to the right of center, in the "hand pick" box arrangement, replacing one of the single one pound bottles of calcium hypochlorite.

Sprinkler Test 9 - Twelve, 30 X 1 Lb. bottles of calcium hypochlorite product, six open "hand pick" arrangement in front and six in cardboard boxes (behind the hand pick) were assembled on the lower shelf of the upper tier. Solid plywood shelving was used to support the lower shelf (and ceiling for tests 1-7). Additionally, six full boxes of commodity, positioned flush with the outside, with six empty cardboard boxes behind, were arranged on an upper level supported by a wire mesh shelf. See Appendix F, Photo 8.

IGNITION: A single half standard ignitor was placed in the lower central right hand - hand pick box arrangement, replacing one of the single one pound bottles of calcium hypochlorite.

Sprinkler Test 10 - LOWER TIER: Eighteen, 30 X 1 Lb. bottles of calcium hypochlorite product in cardboard boxes were assembled on two closed deck wooden pallets in the lower tier of the test enclosure. The boxes were arranged with the stack closest to the flue, three high by three wide to provide a full face of nine full boxes on each pallet as shown in Appendix F, Photo 9. The remainder of the three wide by three deep by three high arrangement was filled with empty boxes (9/27 boxes were full for each of the lower two pallets). The pallets were separated to provide a 6 in. nominal flue with the boxes positioned flush with the pallet's edge defining the flue.

<u>UPPER TIER</u>: A second set of two pallets was positioned on the upper tier supported by steel beams. The only difference between the upper tier and the lower tier was that the upper tier had 10 full boxes of commodity. There were five full boxes for each of the two pallets, arranged in an inverted tee with the central stack, three high and the outer stacks one high each. The remainder of the twenty seven boxes were empty. The pallets were separated to provide a 6 in. nominal flue with the boxes positioned flush with the pallet's edge defining the flue.

IGNITION: Two half standard ignitors were placed at the base of the central stacks of cardboard boxes on the lower tier, positioned on fire bricks.

Sprinkler Test 11 - LOWER TIER: The same arrangement as Sprinkler Test 10, except that the center three boxes on the two pallets from the lower tier had the outer cardboard boxes removed to partially expose the plastic bottles (the retail packaging was left intact).

UPPER TIER:

Same as for Sprinkler Test 10.

IGNITION:

Same as for Sprinkler Test 10.

<u>Sprinkler Test 12</u> - <u>LOWER TIER</u>: The same arrangement as Sprinkler Test 11, except that only the lower tier was used. Also, only five full boxes were used in each of the two pallets, arranged in an inverted tee. The central stack was three high and the outer stacks were only one high at the base, with the remainder of the twenty seven boxes per pallet as empty cardboard.

UPPER TIER:

Not used.

IGNITION:

Same as for Sprinkler Test 10.

Participants of NFPRF's Technical Advisory Committee (TAC) provided the commodity samples as stated herein. Underwriters Laboratories Inc. did not select the samples for test, and subsequently cannot provide any indication of whether they are representative. The results apply only to those samples tested.

3. Test Method

The samples of packaged calcium hypochlorite were placed on two separate 42 in. by 42 in. hard wood pallets. The pallets in tests 5-12 incorporated a nominal 1/2 in. plywood solid top deck. The pallets in tests 1-4 had no solid top deck.

The commodity laden pallets were then placed in the applicable tier of the plywood rack configuration as described above in the samples / set-up section. A nominal 6 in flue space was established in between the pallets when used.

Either three or six automatic sprinklers (as defined above) in the applicable tier were charged with the rated flowing pressure prior to the start of the test. A residual test pressure was established initially to minimize the time lag to obtain the desired test pressure when the automatic sprinklers operated. The sprinkler flow was controlled using a variable speed pump. As the automatic sprinklers operated, the speed of the pump was increased to maintain a constant flowing pressure. Table 6 defines the sprinkler flowing pressure for each test.

The fire was started using a propane torch to ignite the ignitors as defined in the above samples / set-up section.

The test continued until one of the following criteria was met:

- The fire appeared to grow beyond the confines of the enclosure, at which time the water deluge system was activated and the pressure at the operated sprinklers was increased.
- The fire appeared under control and diminished in size, at which time the sprinkler pressure was maintained for at least 5 additional minutes, and then increased to provide extinguishment of the residual fire and dilution of the products of decomposition.

The fire was suppressed prior to commodity involvement based on both visual and thermocouple readings, at which time the sprinkler flow was increased to extinguish the packaging fire.

4. Facility

The fire tests were conducted at UL's large scale fire test facility located in Northbrook, IL.

The test facility cell used to conduct these tests is a nominal 48 ft. by 48 ft. room with a nominal 60 ft. ceiling.

The test room is equipped with an exhaust system capable of being adjusted from near zero flow to 60,000 cubic feet per minute through a 25 foot diameter smoke collection hood to a smoke abatement system. Combustion air is provided through four inlet ducts positioned along the walls of the test facility. The combustion air is introduced into the room approximately 4 feet above floor level. This ventilation arrangement provides adequate air supply so that the fire growth occurs naturally.

5. General Test Conditions

A rack structure consisting of two vertical steel trusses connected by four nominal 8 foot steel beams was constructed for these tests. Nominal 1/2" thick plywood was used to construct two storage bays within this rack arrangement.

Each storage bay consisted of a five sided enclosure to store the pool chemical commodity under test. Both the lower and upper enclosures were used for the tests described herein.

The top of each enclosure incorporated steel beams for structural support. The beam on the front of the assembly also served to retain a hot gas layer within the enclosure (see Appendix F, Photo 1). The seams in the plywood construction were sealed using aluminum tape to better retain the heat and provide for faster sprinkler operation.

6. Water Supply/Rack Sprinkler System

Two manifolds were constructed of nominal 2 in. galvanized steel pipe. Reducing tees (2 in. by 2 in. by 3/4 in.) were provided at each of the six sprinkler locations for each enclosure.

The distance between the three sprinklers on a branchline was 46 in. center to center with the center of the two branchlines being 24 in. apart. The deflectors of the upright automatic sprinklers were nominally 2 in. below the top of the lower plywood enclosure. The distance between the sprinklers and the inner walls of the plywood construction was nominally 1-1/2 in. (See Figure 3). The distance between the

centerline of the pipe and the "inside surface" of the beam was nominally 3-1/2 inches. (See Appendix D, Illustration 2)

7. Sprinklers

The sprinklers used in this investigation were UL Listed 17/32 in. orifice (K factor = 8.0) upright style quick response sprinklers having 3/4 in. NPT thread. These sprinklers incorporated a 3 mm, 155 °F (68°C) temperature rated glass bulb for the thermal sensing element.

8. Ignition Source

Two half standard cellulose cotton rolls soaked in 4 oz. of gasoline and tied in a polyethylene bag were used for each test (except as stated in the samples / set-up as applicable). The dimensions of the half standard ignitors are a nominal 3 in. diameter and 3 in. length.

9. Instrumentation

Calibrated pressure transducers and magnetic flowmeters were used to maintain the required sprinkler discharge during the course of the test. The pressure transducers were located outside the plywood test enclosure.

Inconel sheathed 0.0625 inch chromel alumel thermocouples (TCs) were positioned near each sprinkler to get wet upon sprinkler activation. This provided indication of sprinkler operation time. The TCs were positioned away from the fire's origin so as to not effect the water distribution.

See Figure 3 for sprinkler TC designations as they relate to the graphs of temperature versus time (See Appendix C).

The heat flux across the aisle was measured with a Schmidt-Boelter type total heat flux gage. The flux gage was nominally 7 ft. from the center of the test bay. The heat flux gage had a 30° viewing angle and a maximum range of up to 200 kW/m².

10. Results

The results of the Intermediate Scale rack storage fire tests for oxidizing pool chemicals are as follows. The sprinkler operation timing and test pressure are contained in Table 6 (see Figure 3 for thermocouple designations).

- a) General Observations
- (1) It was observed that when the center sprinkler closest to the outside rack beam activated, it provided a water curtain effect due to impingement on the outside beam.
- (2) Sprinkler Tests 1 and 11 were terminated early by the backup water deluge system due to lack of control by the sprinkler system.

Note that Sprinkler Test 1 was repeated as Sprinkler Test 2 in the same configuration, after post test analysis of Sprinkler Test 1 indicated minimal damage to the test structure and commodity.

Sprinkler Test 11 was terminated early by having the backup water deluge system activate in order to suppress the fire. The plywood test enclosure showed signs of charring to the lower level (see Appendix F, Photo 10) rear wall after the test, however no breach was noted.

- (3) The remainder of the tests showed at least some degree of control of the fire from the standpoint of containment within the test enclosure. In no tested case did the fire breach the test enclosure.
- (4) Sprinkler Tests 6 and 7 demonstrated that the resulting cardboard fire was sufficient to activate the sprinklers prior to commodity becoming involved.
- (5) Sprinkler Test 4 demonstrated that the resulting plastic fire was sufficient to activate the sprinklers prior to commodity becoming involved.
- (6) There was no damage to the cardboard boxes across the 8' aisle target (Sprinkler Tests 1-7 and 12). These targets were not used in tests when commodity was stored in the upper tier.
- (7) It was observed during Sprinkler Tests 1 and 2, the plastic buckets had breached on the bottom due to fire impingement and eventual burn-through of the bottom of the commodity container. This caused commodity to spill on the floor underneath the pallet and caused additional damage to the commodity.
- b) Damage Assessment

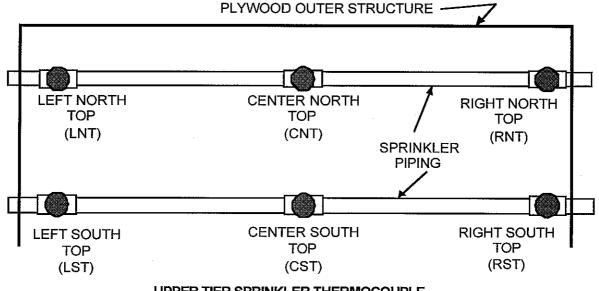
See Appendix D for details of the damage assessment for a particular test.

Photos of damage assessment appear in Appendix F, Photos 11-14.

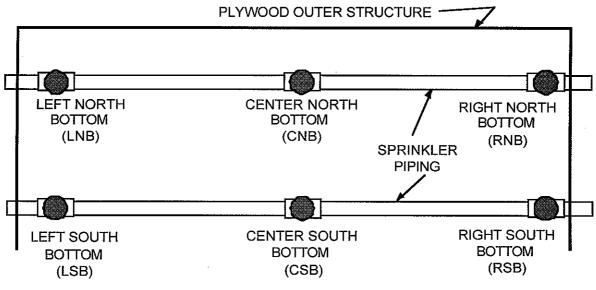
TABLE 6 - Sprinklered Test Results

SPRINKLERED TEST	NUMBER OF OPERATIONS	SPRINKLER DESIGNATIONS	ACTIVATION TIME (min:sec)	SPRINKLER PRESS., PSIG
1*	0	CNB	2:23	50
2	2	CSB	2:18	50
		CNB	2:18	
3	3	CSB	0:31	50
		RSB	3:10	-
		LSB	3:17	
4	1	CSB	0:47	50
5	2	CSB	1:42	25
		CNB	1:42	
6	1	CNB	0:31	50
7	1	CNB	0:24	25
8	1	CST	1:16	50
9	4	CST	1:09	25
		RST	4:51	
		LST	6:10	
		LNT	6:10	
10	1	CNT	0:33	25
11**	6	CNT	0:35	25
1 1		${\tt LNT}$	0:50	
		RNT	0:50	
		LST	1:01	
		CST	0:58	
		RST	1:01	
12	6	CSB	0:33	25
		CNB	0:33	
		RSB	2:37	
]		LSB	2:43	
	}	LNB	2:40	
		RNB	2:37	

^{*} TEST 1 TERMINATED AT 2:23 DUE TO PERCEIVED EXCESSIVE PRODUCT INVOLVEMENT. ** TEST 11 TERMINATED AT 1:05 DUE TO EXCESSIVE PRODUCT INVOLVEMENT.



UPPER TIER SPRINKLER THERMOCOUPLE LOCATIONS (CUT-AWAY PLAN VIEW)



LOWER TIER SPRINKLER THERMOCOUPLE LOCATIONS (CUT-AWAY PLAN VIEW)

FIGURE 3-THERMOCOUPLE DESIGNATIONS

c) Specific Observations

Sprinkler Test 1 demonstrated product involvement, however due to the deluge system being activated, sprinkler system suppression of the resulting fire was not demonstrated. There was chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 2 demonstrated product involvement and subsequent sprinkler system suppression of the resulting fire. There was chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 3 demonstrated product involvement. Sprinkler system suppression of the resulting fire was demonstrated with respect to controlling the fire within the test array. There was minimal chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 4 did not demonstrate product involvement. The fire resulting from the ignitor and plastic container involvement was sufficient to activate the sprinklers prior to chemical product becoming involved.

Sprinkler Test 5 demonstrated product involvement. Sprinkler system suppression of the resulting fire was demonstrated with respect to controlling the fire within the test array. There was chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 6 did not demonstrate product involvement. The fire resulting from the ignitor and cardboard box involvement was sufficient to activate the sprinklers prior to chemical product becoming involved.

Sprinkler Test 7 did not demonstrate product involvement. The fire resulting from the ignitor and cardboard box involvement was sufficient to activate the sprinklers prior to chemical product becoming involved.

Sprinkler Test 8 demonstrated product involvement. Sprinkler system suppression of the resulting fire was demonstrated with respect to controlling the fire within the test array. There were boxes of stored commodity that were not affected by the fire. There was chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 9 demonstrated product involvement. Sprinkler system suppression of the resulting fire was demonstrated with respect to controlling the fire within the test array. There were boxes of stored commodity that were not affected by the fire. There was chemical product remaining in the breached containers after the test. No damage to the test enclosure was noted.

Sprinkler Test 10 did not demonstrate product involvement. The fire resulting from the ignitor and cardboard box involvement was sufficient to activate the upper level sprinklers prior to chemical product becoming involved.

Sprinkler Test 11 demonstrated significant product involvement, however due to the deluge system being activated, sprinkler system suppression of the resulting fire was not demonstrated. There was chemical product remaining in the breached containers after the test. Charring of the test enclosure's rear wall of the lower tier was noted (see Appendix F, Photo 10). No breach of the test enclosure was noted.

Sprinkler Test 12 demonstrated product involvement. Sprinkler system suppression of the resulting fire was demonstrated with respect to controlling the fire within the test array. All boxes of stored commodity were affected by the fire. Additional empty containers were charred and breached from the fire. There was chemical product remaining in the breached commodity containers after the test. No further charring of the test enclosure was noted as a result of this last test (as compared with the damage from Sprinkler Test 11).

E. Observations and Conclusions

1. The peak convective heat release rates generated during the large-scale calorimetry fire tests were as follows:

(kW)

•	(****)
Pea gravel filled high density polyethylene 2 lb. capacity containers (considered a Class III or IV commodity)	464
Trichloroisocyanuric Acid (granular) in high density polyethylene 2 lb. capacity containers	649
Trichloroisocyanuric Acid (1 in. tablets) in high density polyethylene	
2 lb. Capacity containers	877
• •	,736
(Considered a Group A plastic)	
Calcium hypochlorite (granular) in 1 lb. surlin bags 6	,696
Calcium hypochlorite (granular) in 1lb. high density polyethylene containers1	6,184

It should be noted that all of the above commodity was cartoned. Also, the convective heat release rates that were measured for calcium hypochlorite in both tests are less than what was actually generated due to spillover from the calorimeter into the test cell.

Based upon the above data and observations made during the fire tests, the following can be stated:

•Trichloroisocyanuric acid (granular and 1 in. tablets) in high density polyethylene 2 lb. capacity containers has a burning rate between a Class III or IV commodity

and a Group A plastic. This pool chemical did not increase the burning rate of the high density polyethylene containers and corrugated fiberboard cartons. Therefore, this commodity does not meet the burning rate portion of the definition for a Class I oxidizer in NFPA 430 as it did not even provide a slight increase in the burning rate.

This material is prone to a slow decomposition in a fire situation. The decomposition temperature per the manufacturer is between 428 $^{\circ}$ F and 482 $^{\circ}$ F (220 $^{\circ}$ C and 250 $^{\circ}$ C).

•Although not part of this research project, it is known that trichloroisocyanuric acid will react and ignite spontaneously when in contact with certain organic liquids. Therefore, based upon the NFPA 430 definitions for oxidizers, this commodity does meet the spontaneous ignition portion of the definition for a Class II oxidizer.

Of particular concern to the fire service, trichloroisocyanuric acid will produce corrosive and toxic gases, such as chlorine, and hydrogen chloride within the white smoke that is produced when burning. Additionally, when water is applied to burning trichloroisocyanuric acid, a denser white smoke is produced as well as nitrogen trichloride. Nitrogen trichloride is a corrosive and unstable material capable of exothermic decomposition. The formation and almost immediate decomposition of the material is accompanied by a loud and rapid "popping" sound as long as water is applied. However, it should be emphasized that the only way to eliminate the formation of nitrogen trichloride and the dense white smoke is to break apart any burning pallet loads of this material and deluge the material with copious quantities of water, such as from a hand held hose line. This will have the effect of reducing the trichloroisocyanuric acid below its decomposition temperature and also extinguish the fire. Any fire fighting activity would of course necessitate wearing the appropriate personal protective equipment and self-contained breathing apparatus.

Fire fighters should be particularly aware of a phenomenon witnessed during a couple of the sprinkler tests where the sprinklers provided a rapid knockdown of the visible fire in the compartment. In such a case there would be strong temptation to shut down the sprinklers and assume the fire was out. However, commodity containers were observed to suddenly flare up strongly, even after several minutes of no visible fire being present, and with the sprinklers still operating.

As a precaution, fire fighters should have charged hand lines in place near the compartment **before** shutting down the sprinklers. Extreme caution should be exercised in overhauling commodity containers which have been exposed to fire, due to the possibility of re-ignition, and also the liberation of noxious gases.

2. Calcium hypochlorite (granular) in 1 lb. surlin bags and 1 lb. high density polyethylene containers produced a severe increase in the burning rate of the surlin bags, high density polyethylene containers, and corrugated fiberboard cartons. It should be noted that the very high heat release rate that was generated was derived from the heat of combustion and the exothermic heat of decomposition. This process was accompanied by the production of a large volume of oxygen and dense white smoke containing chlorine. The oxygen that was produced, as a result of the decomposition process, was generated rapidly and allowed the combustible packaging material and wood slatted pallets to burn in an "oxygen enriched atmosphere." At the core of the burning test array the flame color was white. The combustion/decomposition process accelerated so quickly that the 10 mW large-scale calorimeter was incapable of capturing and measuring the actual heat release rate due to spill-over.

The rapid production of oxygen had the effect of overpressurizing and bursting the surlin bags and high density polyethylene containers which propelled burning packaging material, and decomposing and undecomposed calcium hypochlorite throughout the test cell. Aside from a minor amount of unburned combustible packaging material that was propelled away from the test array, the only appreciable amount of unburned combustible material, at the end of both tests, was the charred remains of the bottom portion of the slatted wood pallets.

The total weight of calcium hypochlorite test commodity in Free-burn Tests 2 and 3, including the two slatted wood pallets, was 1468 lbs. and 1452 lbs., respectively. It is noteworthy that the combustion/decomposition process was over within 2 minutes of ignition in both tests. Based on the results of these tests it would be reasonable to categorize containerized calcium hypochlorite (available chlorine $\hat{\mathbf{U}}$ 68%) as a Class III oxidizer.

3. In-rack automatic sprinkler protection, and barriers used within an open frame rack structure, were found to be effective at mitigating the effects of fires involving containerized calcium hypochlorite (available chlorine $\acute{\rm U}$ 68%). This protection scheme was based upon the concept of "localized protection", without consideration for ceiling sprinkler system design.

The test commodity was placed within a single row rack having 2 rack bays stacked vertically. Each rack bay had dimensions of 96 in. x 42 in. x 62 in. (LWH), giving an overall rack height of 10 ft. 4 in (124 in.) This rack bay was enclosed with 1/2-in thick plywood barrier on the 2 sides, back, and top of the rack. A 1/2-in thick horizontal plywood barrier was placed at a height of 62 in., or over the lower bay, on certain tests as indicated below. The aisle facing side was open.

Below the top, and intermediate horizontal barrier, when used, 2 parallel lines of in-rack sprinklers were placed with each line having 3 sprinklers, for a total of 6

sprinklers per bay. The in-rack sprinkler piping was located 12 in. from the lengthwise centerline of the rack bay.

The sprinklers, which were located at the vertical rack uprights and mid-bay, were upright, 17/32 in., K=8.0, 155 °F rated, and had an RTI of 50. Tests were conducted using sprinkler head pressures of either 50 or 25 psig. This protection scheme was found to be effective with the following:

- Uncartoned 70 lb. pails of calcium hypochlorite placed on slatted (Sprinkler Test 2) and solid wood pallets (Sprinkler Test 5) in the lower bay. Horizontal barrier and 6 in-rack sprinklers were placed at 62 in. level.
- Cartoned 1 lb. bottles (30 bottles/carton) of calcium hypochlorite placed on Sprinkler Test 3) and solid wood pallets (Sprinkler Test 12) in lower bay. Horizontal barrier and 6 in-rack sprinklers were placed at 62 in. level.
- Case-cut 1 lb. bottles (30 bottles/carton) of calcium hypochlorite placed on top
 of horizontal barrier at 62 in. level and cartoned 1 lb. bottles (30 bottles/carton)
 of calcium hypochlorite placed on top of wire mesh shelf at 93 in. level. Six inrack sprinklers were placed at 124 in. level. below the top horizontal barrier
 (Sprinkler Tests 8 & 9).

Sprinkler Test 1 was inadvertently terminated as a precautionary measure and was repeated as Sprinkler Test 2.

Sprinkler Test 11, which had cartoned 1 lb. bottles (30 bottles/carton) of calcium hypochlorite placed on solid wood pallets in the upper and lower bays with 6 inrack sprinklers placed below the top horizontal barrier, or 124 in. level., was an uncontrolled fire test. Calcium hypochlorite decomposition was induced by removing fiberboard cartons and placing ignitor against the high density polyethylene bottles.

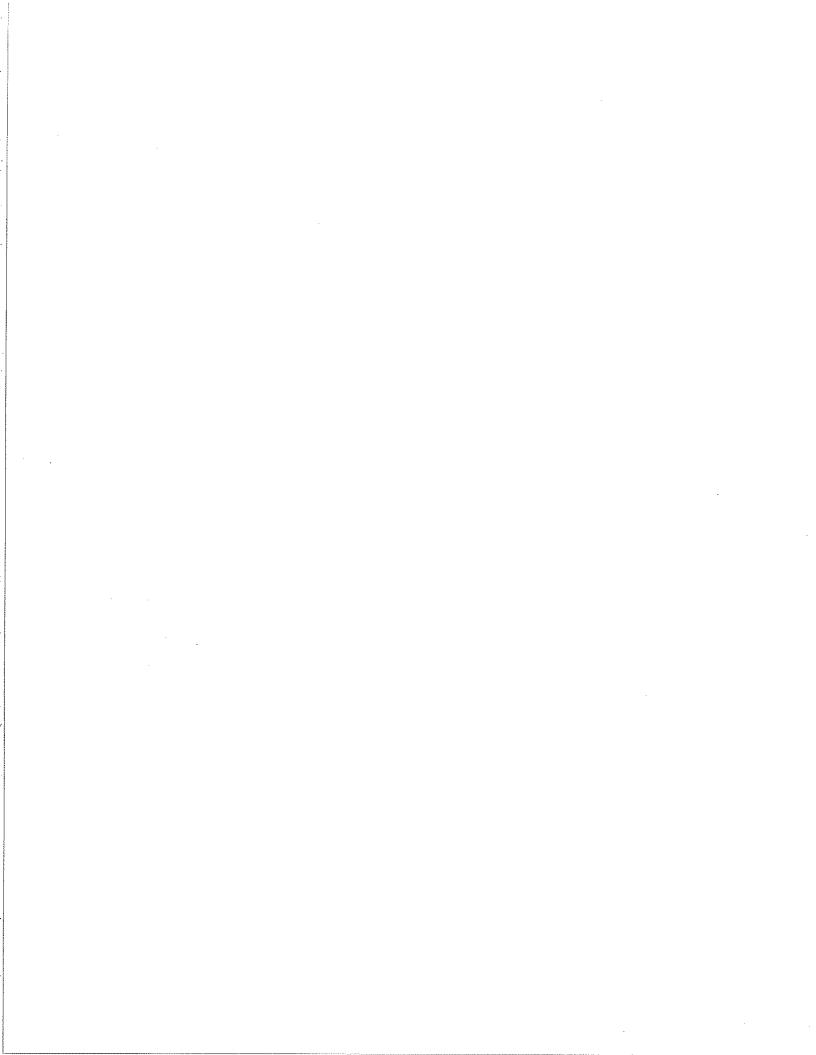
Sprinkler Test 4 (70 lb. pails) and Sprinkler Tests 6,7, & 10 (cartoned 1 lb. bottles) did not involve calcium hypochlorite decomposition. For the purpose of these tests, calcium hypochlorite decomposition was considered desirable as it presented a "worst-case" scenario. Sprinkler Tests 4, 6, 7, & 10 had fires that only involved packaging material.

Typical slotted wood pallets were initially used in the tests. However, early observations indicated that the slotted pallets allowed fire to burn underneath them. This fire activity was largely shielded from the water discharge of the sprinklers. The fire under the pallet directly attacked the bottom of the commodity container(s). Shielded from the sprinkler spray the fire would burn through the exposed bottom of the commodity container and then burrow into the container increasing the fire intensity.

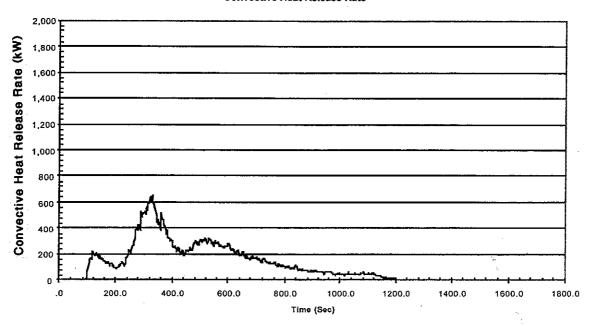
Consequently, solid top wood pallets were used to prevent this phenomenon and did so sucdessfully.

APPENDIX A

CONVECTIVE HEAT RELEASE RATE RESULTS

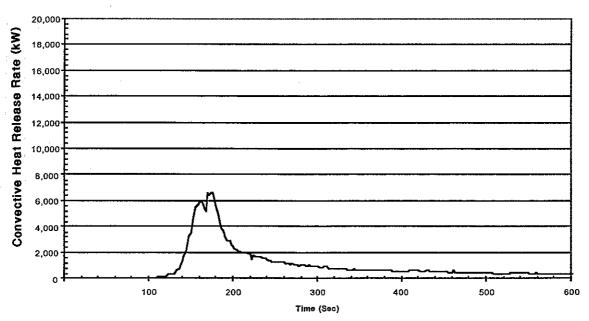


NFPRF
Two Half Pallets of Trichloro-s-Triazinetrione
Convective Heat Release Rate



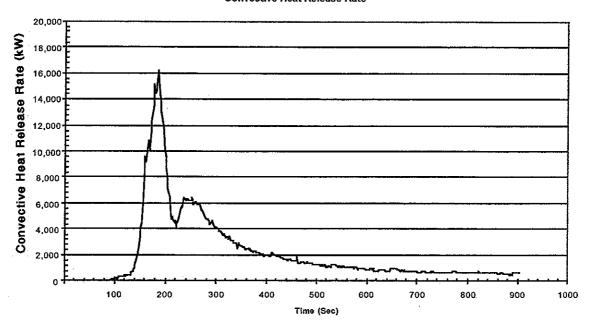
Test 1

NFPRF Two Half Pallets of Calcium Hypochlorite Convective Heat Release Rate



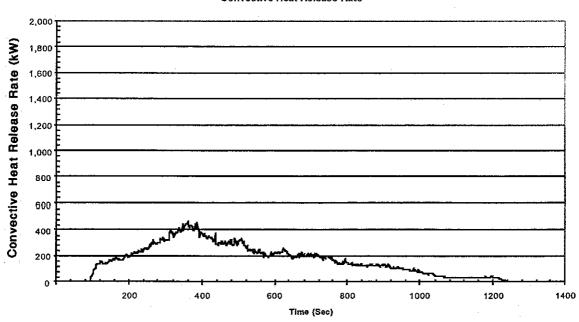
Test 2

NFPRF
Two Half Pallets of Calcium Hypochlorite
Convective Heat Release Rate



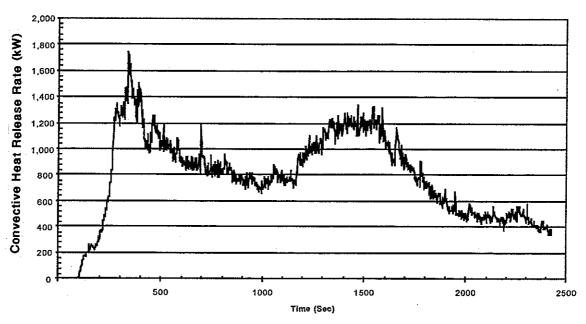
Test 3

NFPRF
Two Half Pallets of Pea Gravel
Convective Heat Release Rate



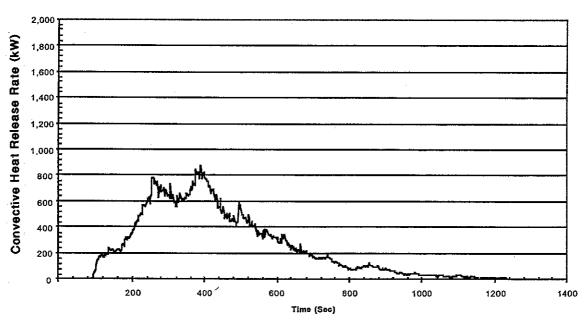
Test 4

NFPRF
Two Half Pallets of Empty Plastic Containers in Corrugated Cartons
Convective Heat Release Rate



Test 5

NFPRF
Two Half Pallets of Trichloro-s-Triazinetrione
Convective Heat Release Rate



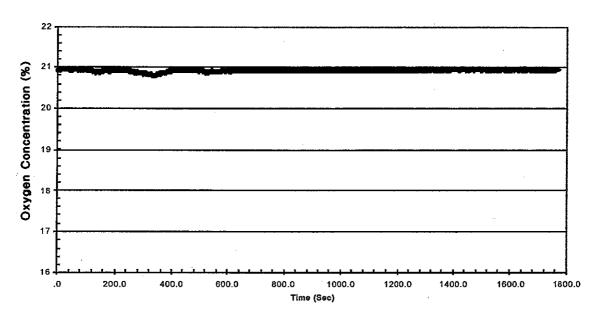
Test 6



APPENDIX B OXYGEN CONCENTRATIONS

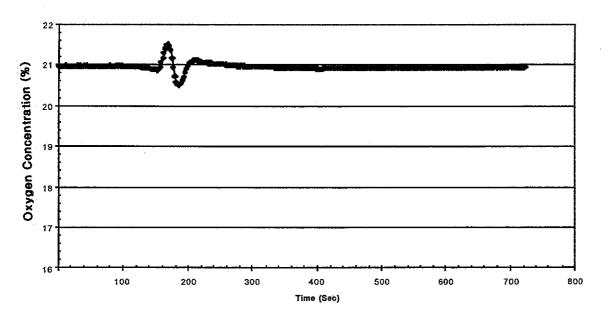
-				
•				

NFPRF
Two Half Pallets of Trichloro-s-Triazinetrione
Oxygen Concentration



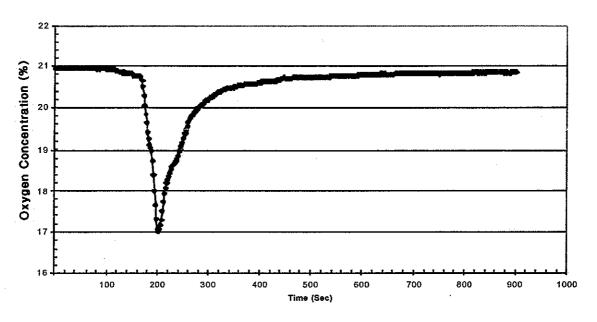
Test 1

NFPRF
Two Half Pallets of Calcium Hypochlorite
Oxygen Concentration



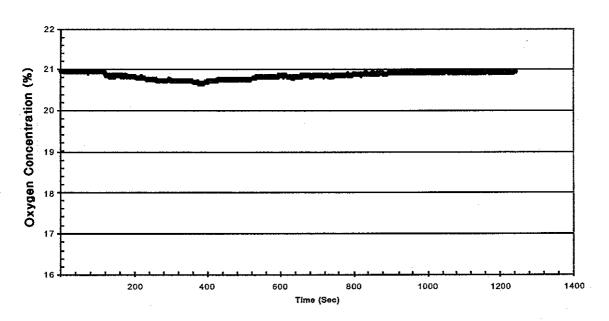
Test 2

NFPRF
Two Half Pallets of Calcium Hypochlorite
Oxygen Concentration



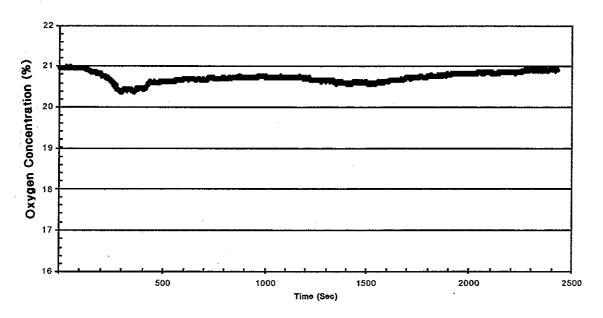
Test 3

NFPRF
Two Half Pallets of Pea Gravel
Oxygen Concentration



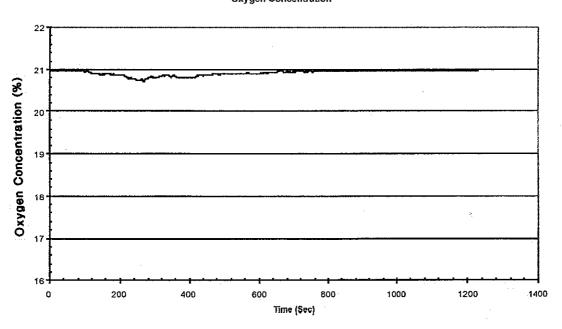
Test 4

NFPRF
Two Half Pallets of Empty Plastic Containers in Corrugated Cartons
Oxygen Concentration

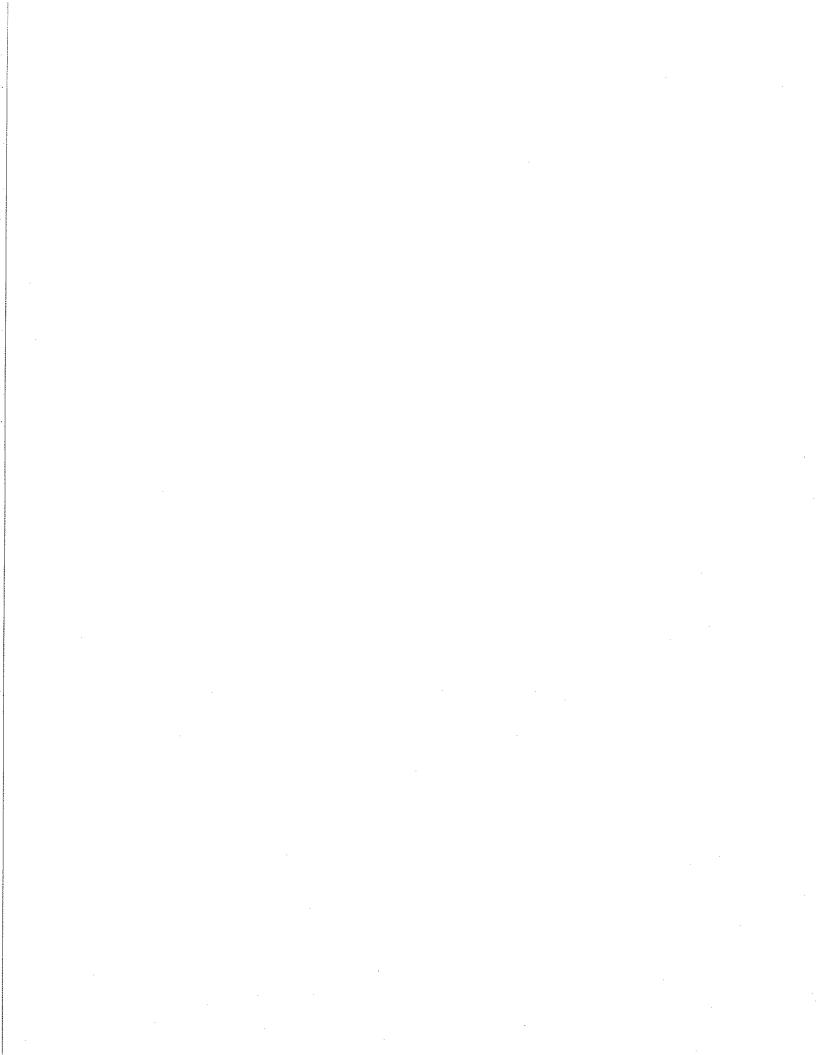


Test 5

NFPRF
Two Half Pallets of Trichloro-s-Triazinetrione
Oxygen Concentration

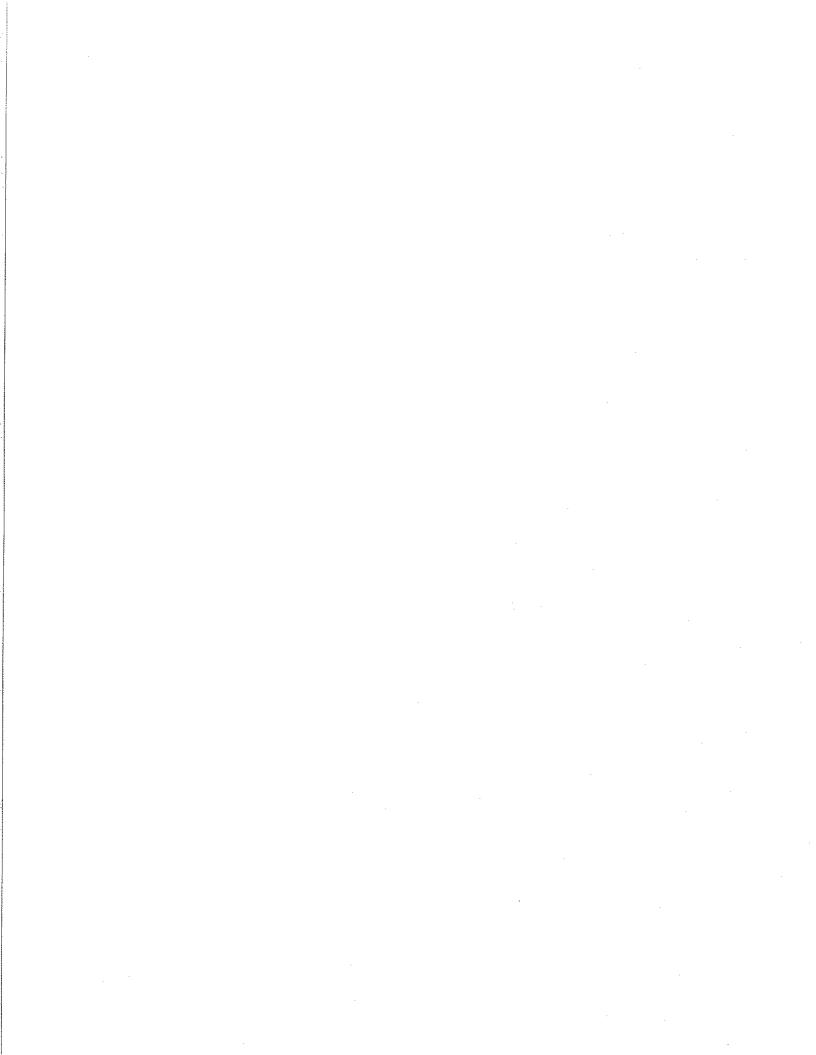


Test 6



APPENDIX C

THERMOCOUPLE and RADIOMETER GRAPHS



NFPRF - TEST #1 Calcium Hypo Chlorite 70 lb pails - x4 SOUTH BOTTOM TCS

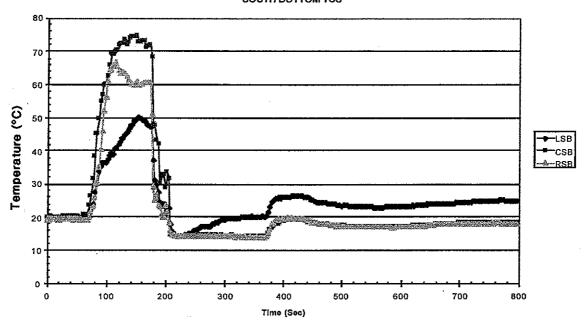


Illustration 1.

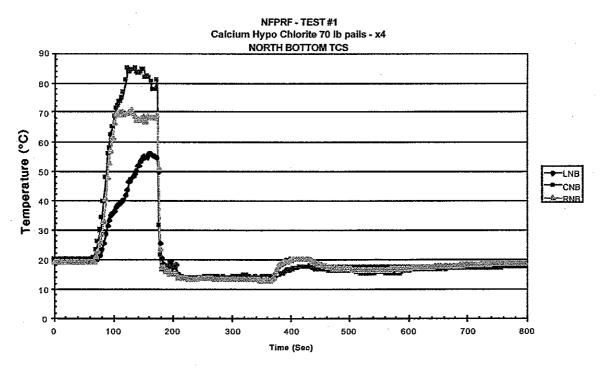


Illustration 2.

NFPRF - TEST #1 Calcium Hypo Chlorite 70 lb pails - x4 RADIANT HEAT FLUX ACROSS AISLE

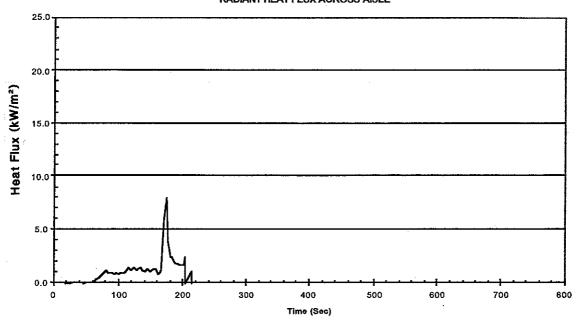


Illustration 3.

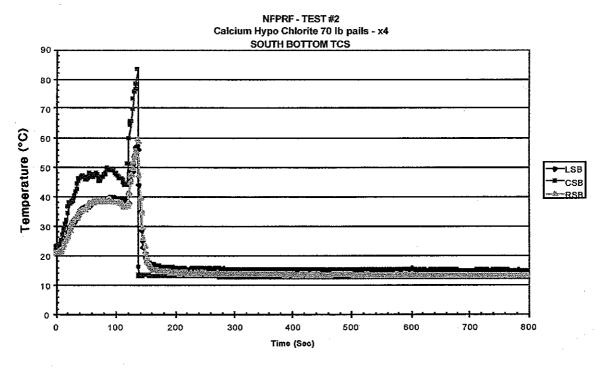


Illustration 4.

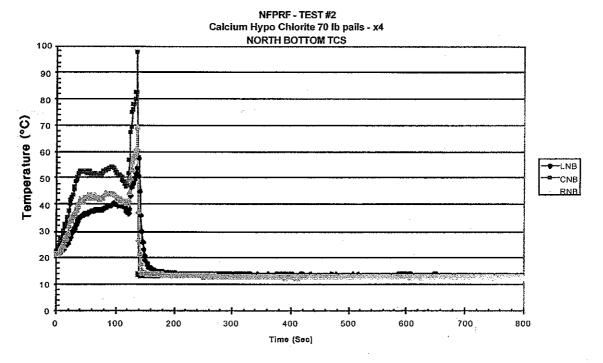


Illustration 5.

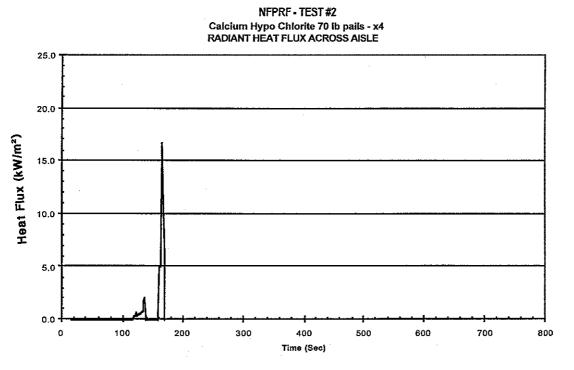


Illustration 6.

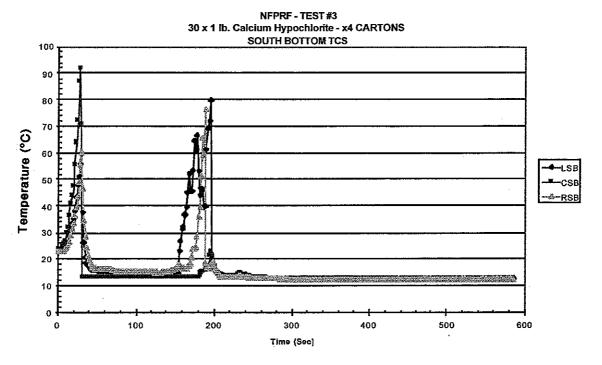


Illustration 7.

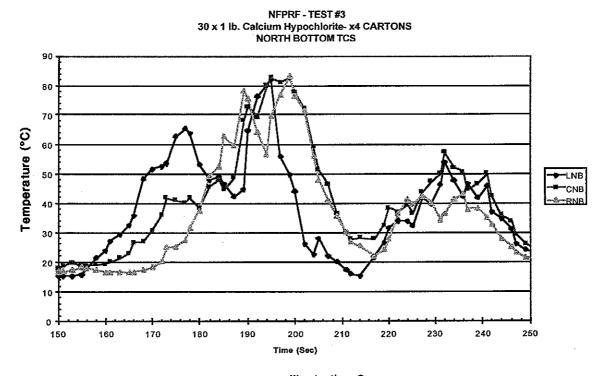


Illustration 8.

NFPRF - TEST #3 30 x 1 lb. Calcium Hypochlorite - x4 CARTONS RADIANT HEAT FLUX ACROSS AISLE

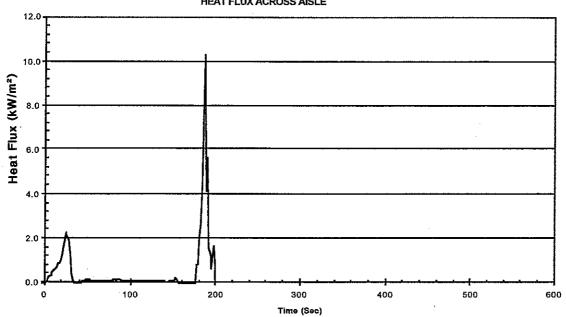


Illustration 9.

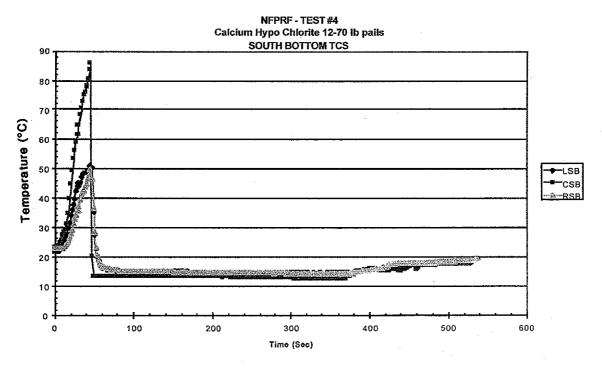


Illustration 10.

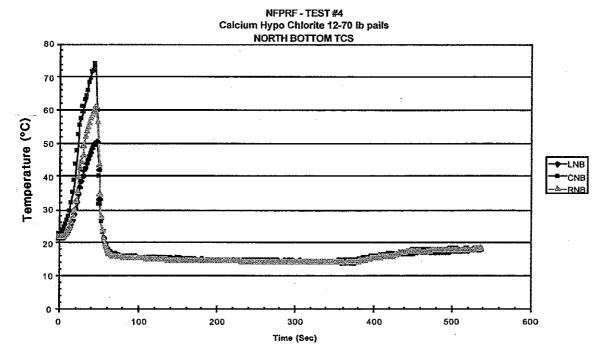


Illustration 11.

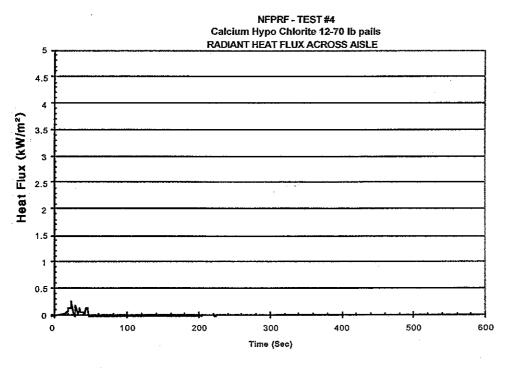


Illustration 12.

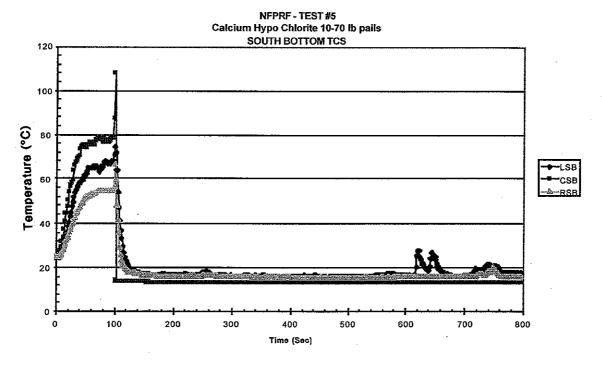


Illustration 13.

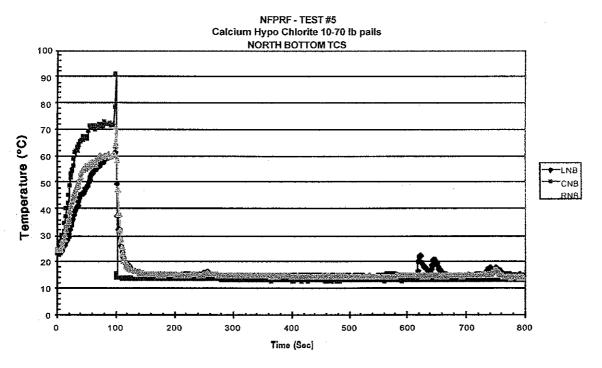


Illustration 14.

NFPRF - TEST #5
Calcium Hypo Chlorite 10-70 lb pails
RADIANT HEAT FLUX ACROSS AISLE

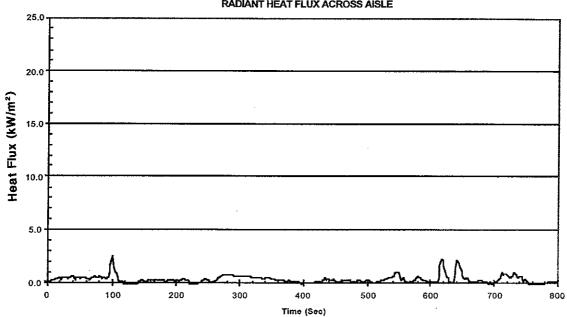


Illustration 15.

NFPRF - TEST #6 30 x 1 Lb. Calcium Hypochlorite - 10 Cartons SOUTH BOTTOM TCS

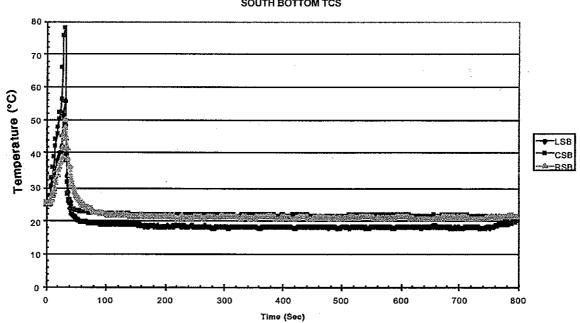


Illustration 16.

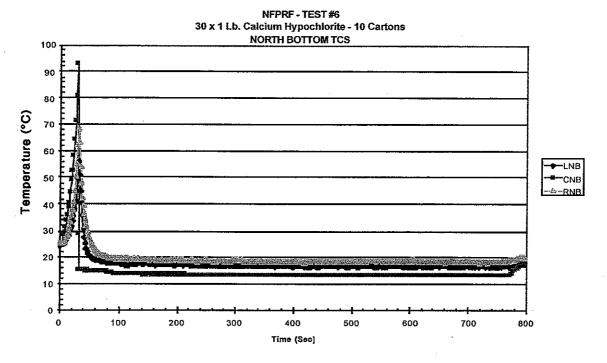


Illustration 17.

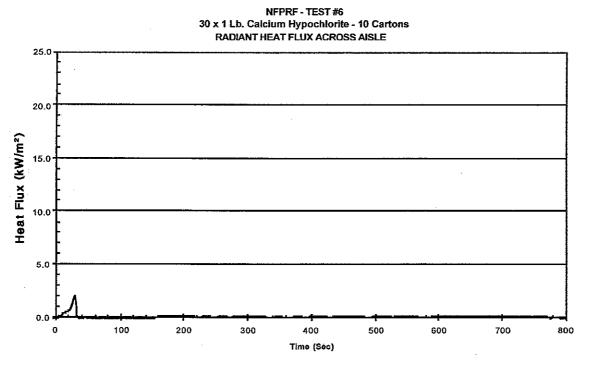


Illustration 18.

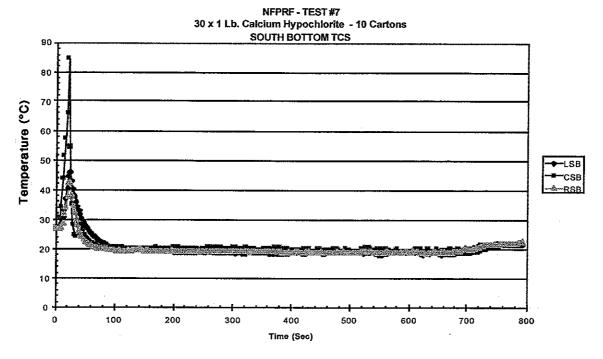


Illustration 19.

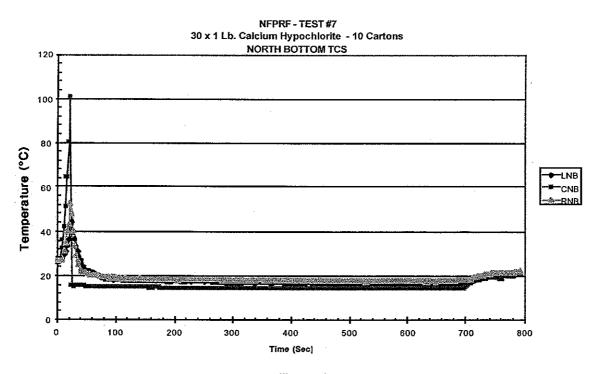


Illustration 20.

NFPRF - TEST #7
30 x 1 Lb. Calcium Hypochlorite - 10 Cartons
RADIANT HEAT FLUX ACROSS AISLE

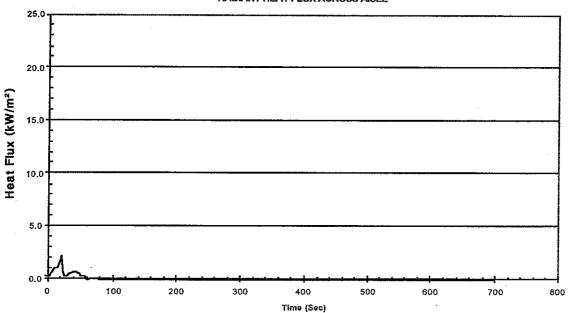


Illustration 21.

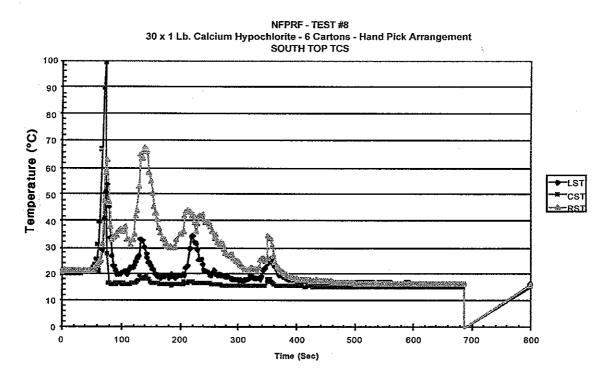


Illustration 22.

NFPRF - TEST #8
30 x 1 Lb. Calcium Hypochlorite - 6 Cartons - Hand Pick Arrangement
NORTH TOP TCS

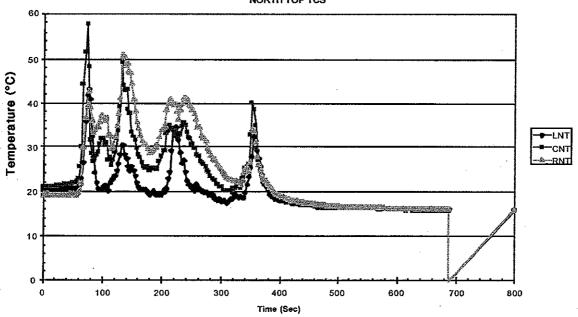


Illustration 23.

NFPRF - TEST #8
30 x 1 Lb. Calcium Hypochlorite - 6 Cartons - Hand Pick Arrangement
RADIANT HEAT FLUX ACROSS AISLE

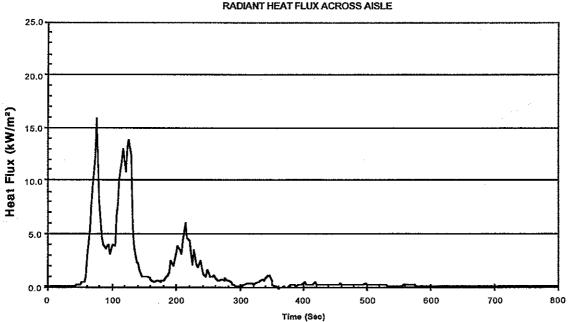


Illustration 24.

NFPRF - TEST #9 30 x 1 Lb. Calcium Hypochlorite - 18 Cartons - Hand Pick Arrangement SOUTH TOP TCS

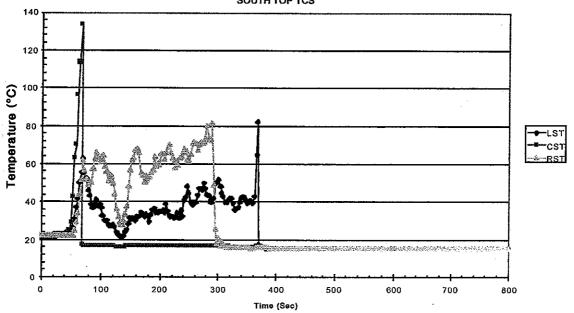


Illustration 25.

NFPRF - TEST #9
30 x 1 Lb. Calcium Hypochlorite - 18 Cartons - Hand Pick Arrangement
NORTH TOP TCS

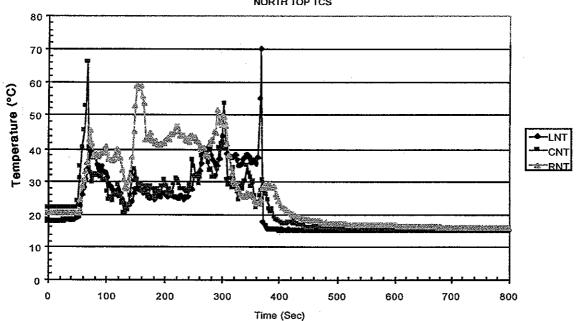


Illustration 26.

NFPRF - TEST #9
30 x 1 Lb. Calcium Hypochlorite - 18 Cartons - Hand Pick Arrangement
RADIANT HEAT FLUX ACROSS AISLE

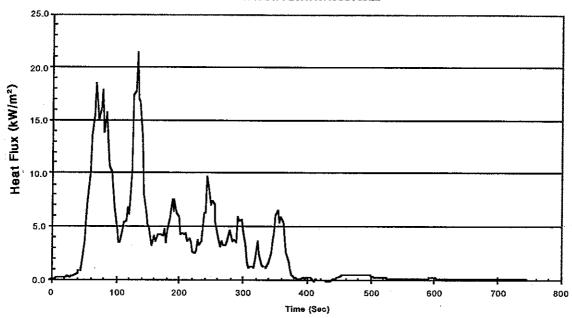


Illustration 27.

NFPRF - TEST #10
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Arrangement
SOUTH TOP TCS

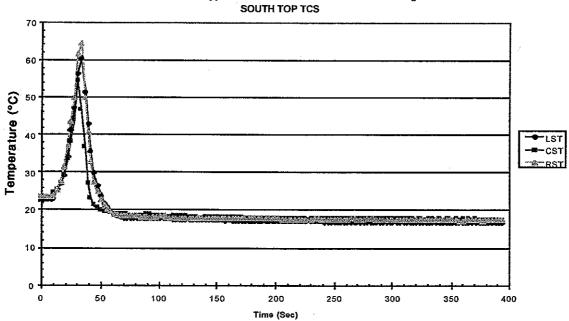


Illustration 28.

NFPRF - TEST #10
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Arrangement
NORTH TOP TCS

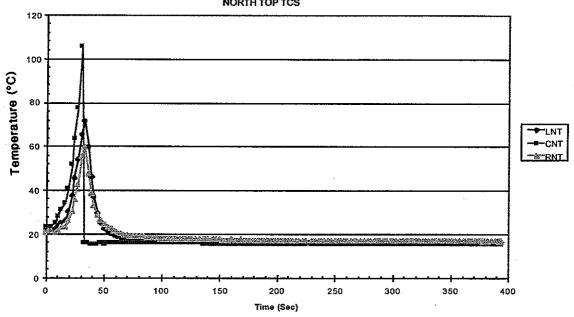


Illustration 29.

NFPRF - TEST #10
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Arrangement
RADIANT HEAT FILLY ACROSS AISLE

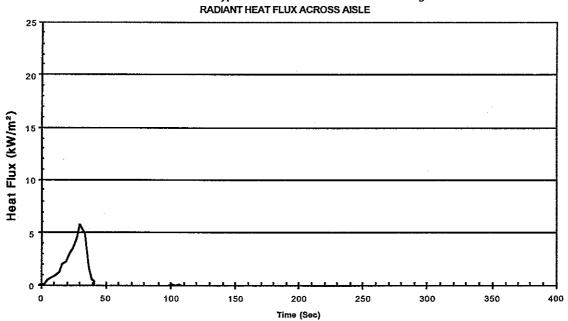


Illustration 30.

NFPRF - TEST #11
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Exposed Arrangement SOUTH TOP TCS

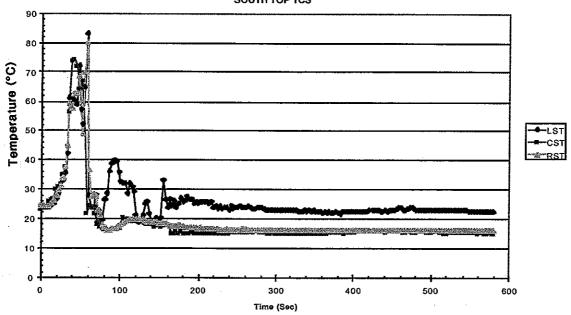


Illustration 31.

NFPRF - TEST #11
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Exposed Arrangement
NORTH TOP TCS

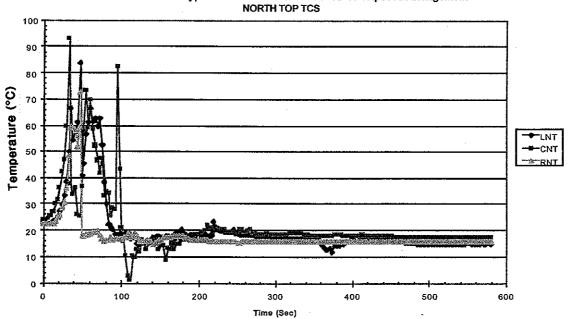


Illustration 32.

NFPRF - TEST #11
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Exposed Arrangement
SOUTH BOTTOM TCS

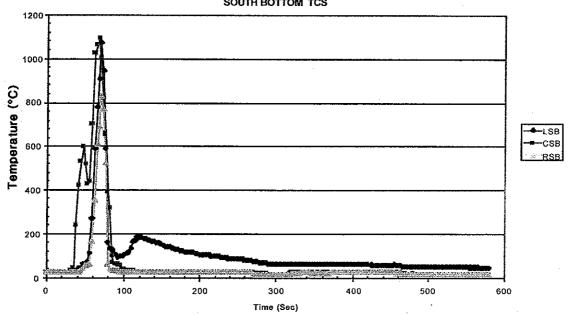


Illustration 33.

NFPRF - TEST #11
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Exposed Arrangement

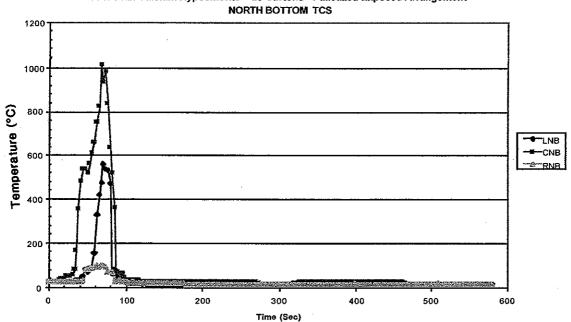


Illustration 34.

NFPRF - TEST #11
30 x 1 Lb. Calcium Hypochlorite - 28 Cartons - Palletized Exposed Arrangement
RADIANT HEAT FLUX ACROSS AISLE

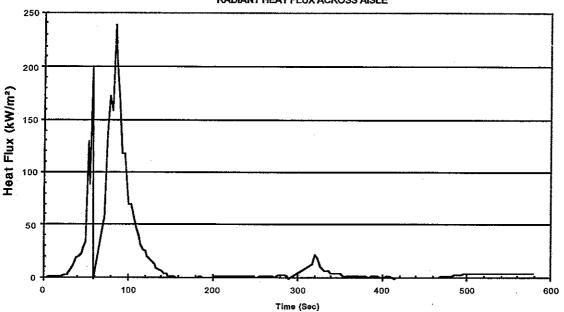


Illustration 35.

NFPRF - TEST #12
30 x 1 Lb. Calcium Hypochlorite - 10 Cartons - Palletized Exposed Arrangement
SOUTH BOTTOM TCS

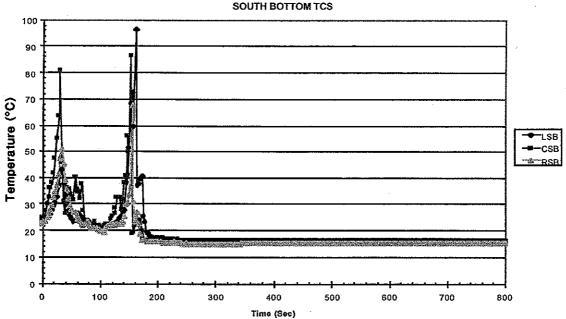


Illustration 36.

NFPRF - TEST #12

30 x 1 Lb. Calcium Hypochlorite - 10 Cartons - Palletized Exposed Arrangement

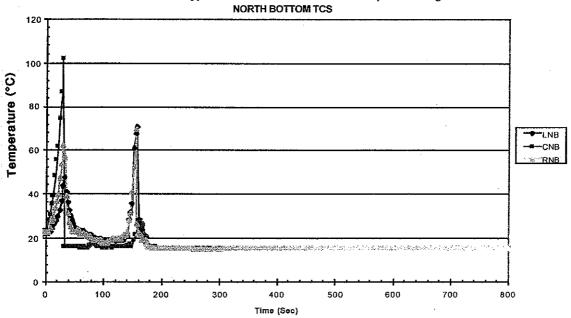


Illustration 37.

NFPRF - TEST #12 30 x 1 Lb. Calcium Hypochlorite - 10 Cartons - Palletized Exposed Arrangement RADIANT HEAT FLUX ACROSS AISLE

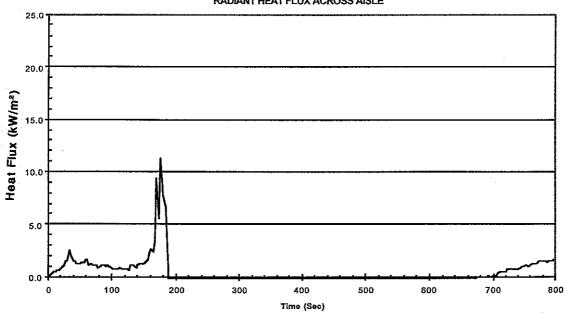
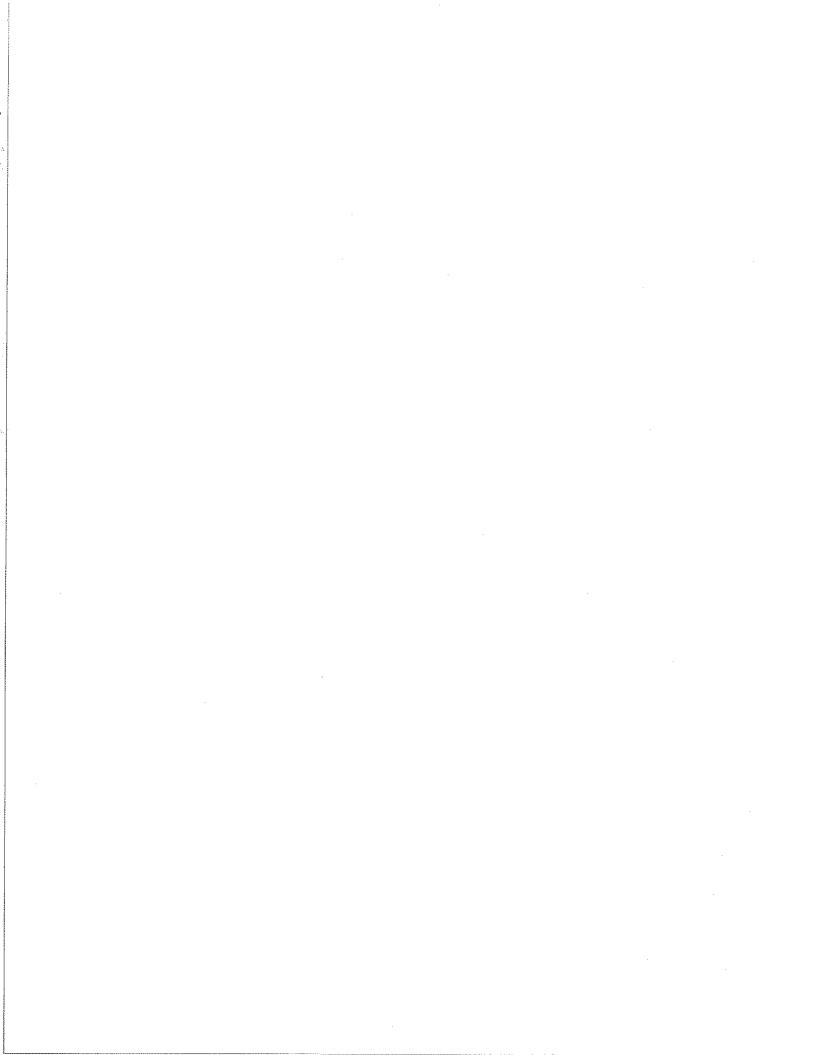


Illustration 38.



APPENDIX D DAMAGE ASSESSMENT SCHEMATICS

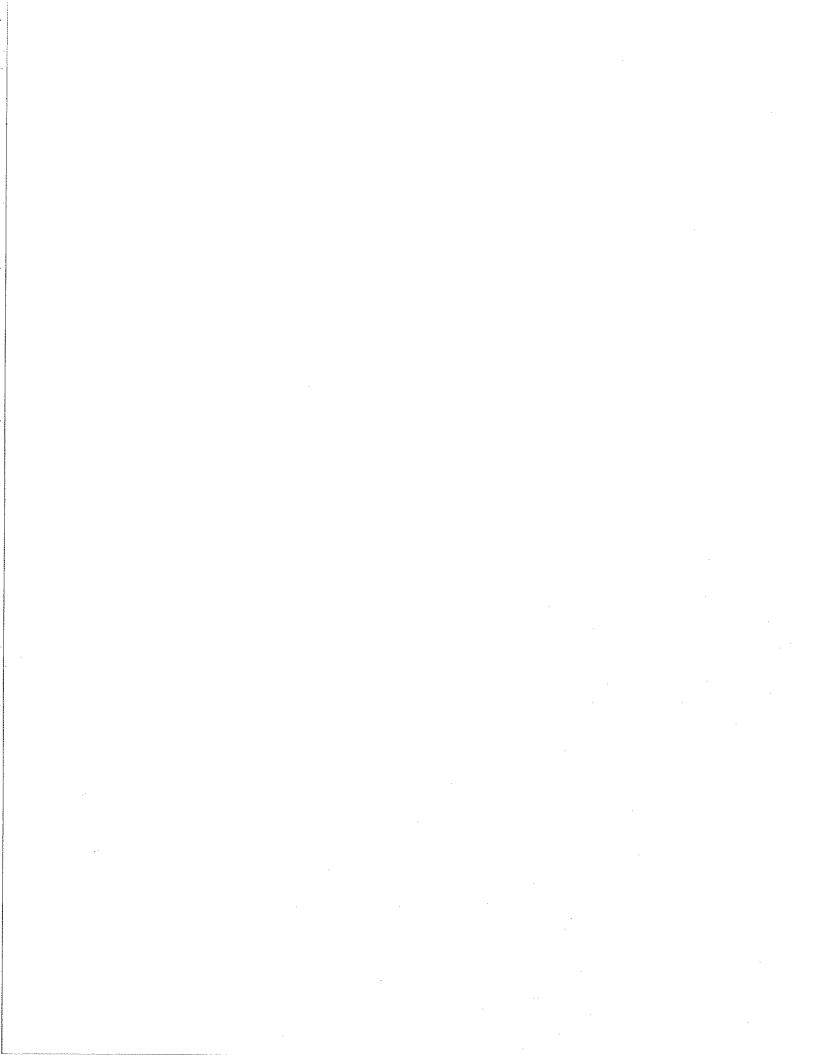


ILLUSTRATION 1 General Test Structure Configuration

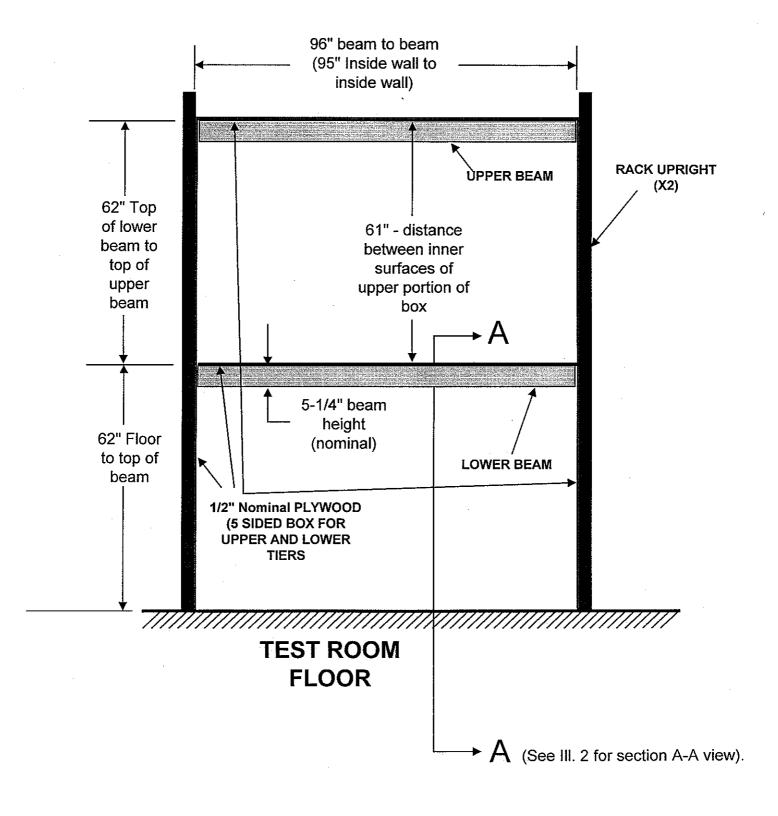
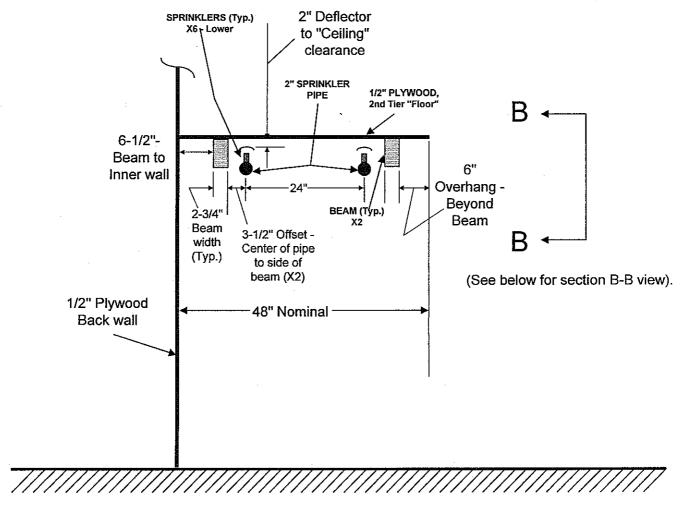
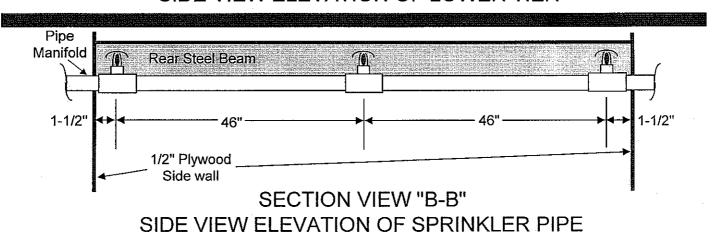


ILLUSTRATION 2 Piping Details



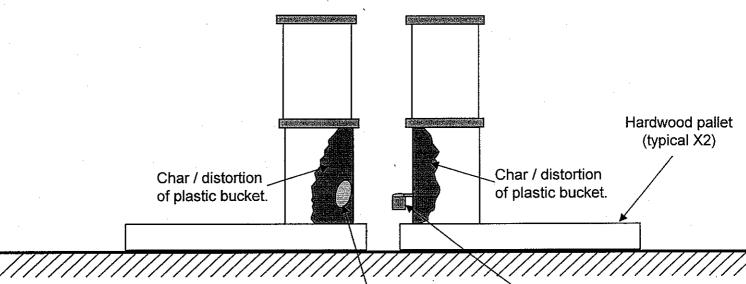
TEST ROOM FLOOR

SECTION VIEW "A-A" SIDE VIEW ELEVATION OF LOWER TIER



SPRINKLER TEST #1 DAMAGE ASSESSMENT

<u>Commodity</u>: Four, 70 pound buckets of calcium hypochlorite product.



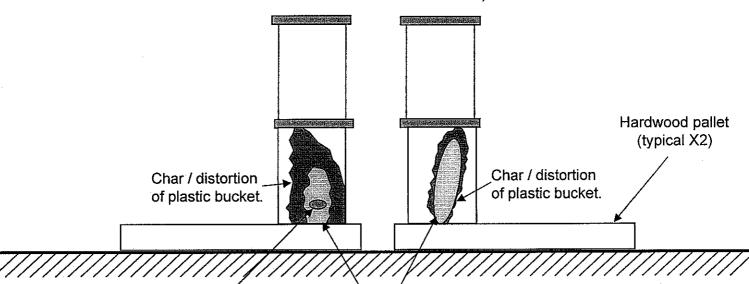
Hole burned into bucket with scoop inside. Product remaining inside.

Noticeable scoop fused to outside of bucket. Product remaining inside.

SPRINKLER TEST #2 DAMAGE ASSESSMENT

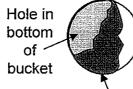
Commodity: Four, 70 pound buckets of calcium hypochlorite product.

(LOWER BUCKET VIÈW ROTATED OUT FOR CLARITY OF ASSESSMENT)



Scoop visible (flush with bucket).

Hole with product remaining inside.

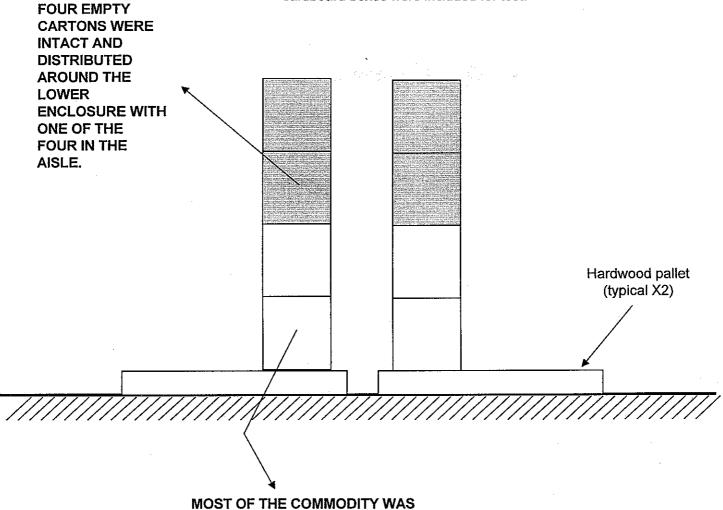


Plastic Char

Bottom view of left bucket

SPRINKLER TEST #3 DAMAGE ASSESSMENT

Commodity: Four, 30 X 1 Lb. plastic containers of calcium hypochlorite product in cardboard containers (inner and outer). Four additional empty cardboard boxes were included for test.



CONSUMED DURING THE TEST.

KEY:

ONLY COLLAPSED REMAINS OF CARDBOARD AND WETTED POWDER WERE EVIDENT AFTER THE TEST.

FULL **EMPTY TARGET COMMODITY BOX** BOX

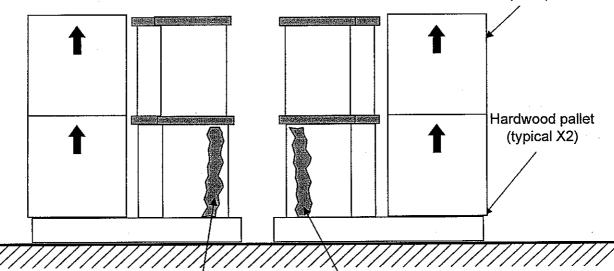
SPRINKLER TEST #4 DAMAGE ASSESSMENT

Commodity: Twelve, 70 pound buckets of

calcium hypochlorite product (2 high, 6 on each pallet).

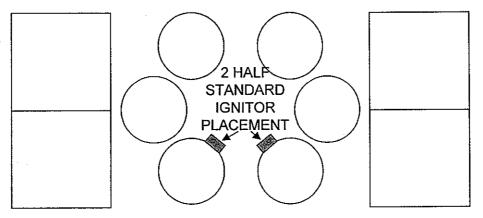
(LOWER OUTER BUCKET VIEW ROTATED OUT FOR CLARITY OF ASSESSMENT)

Empty Standard Group A Cardboard Boxes (8 altogether - to fill pallet)



Char of plastic bucket (lower bucket only affected). Char of plastic bucket (lower bucket only affected).

SIDE VIEW OF COMMODITY ARRANGEMENT



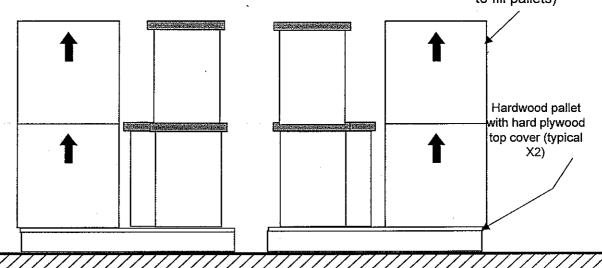
TOP VIEW OF COMMODITY

SPRINKLER TEST #5 DAMAGE ASSESSMENT

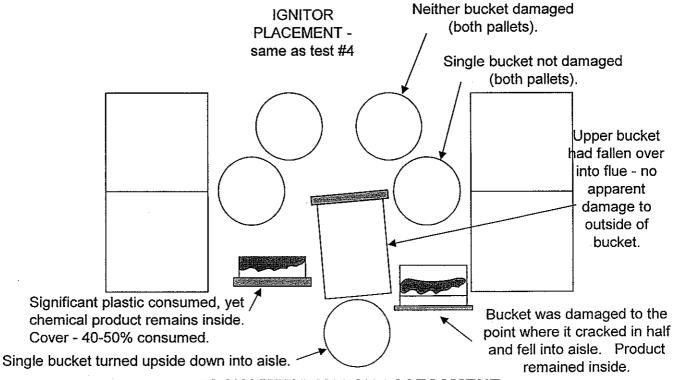
Commodity: Ten, 70 pound buckets of

calcium hypochlorite product (2 high each on outside, 1 high in center - 5 on each pallet).

Empty Standard Group A Cardboard Boxes (8 altogether - to fill pallets)

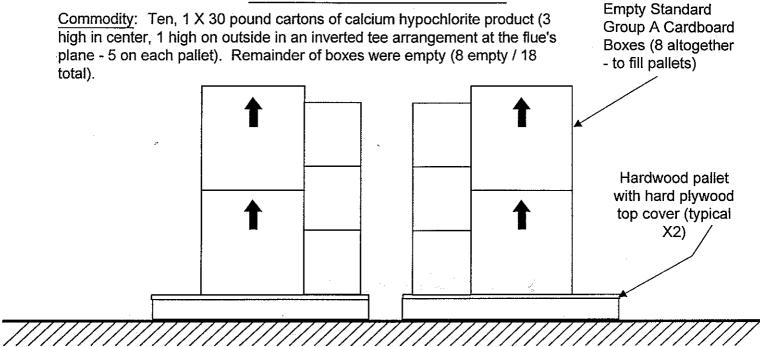


SIDE VIEW OF COMMODITY ARRANGEMENT

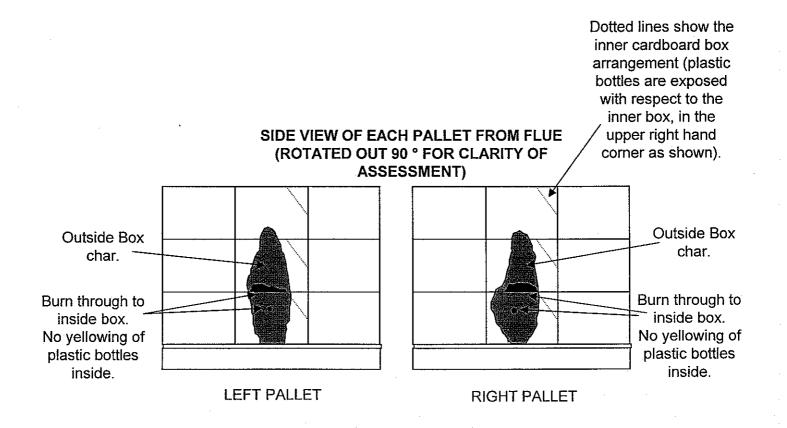


PLAN VIEW DAMAGE ASSESSMENT

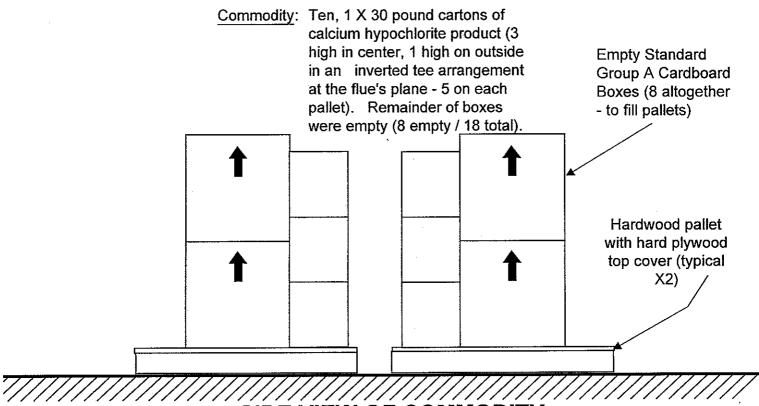
SPRINKLER TEST #6 DAMAGE ASSESSMENT



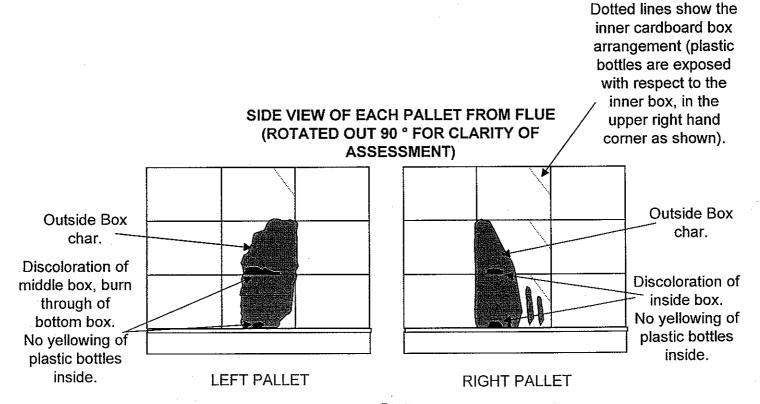
SIDE VIEW OF COMMODITY ARRANGEMENT



SPRINKLER TEST #7 DAMAGE ASSESSMENT



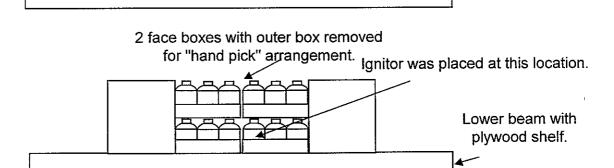
SIDE VIEW OF COMMODITY ARRANGEMENT



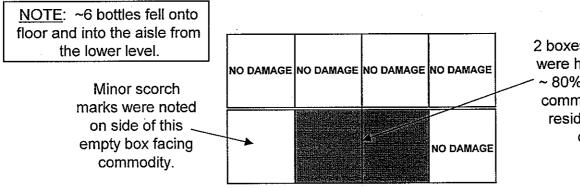
SPRINKLER TEST #8 DAMAGE ASSESSMENT

Commodity: Lower level - Four, 1 X 30 pound cartons of calcium hypochlorite product (2 open "hand pick" style at front and 2 with outer cardboard remaining) with 4 empty boxes.

> Upper level - Two, 1 X 30 pound cartons of calcium hypochlorite product centered at the front with outer cardboard remaining, and 6 empty boxes flanking.



SIDE VIEW OF COMMODITY **ARRANGEMENT**



2 boxes with commodity were heavily damaged. ~80% consumption of commodity with noted residual powder not consumed.

Upper beam with wire mesh screen.

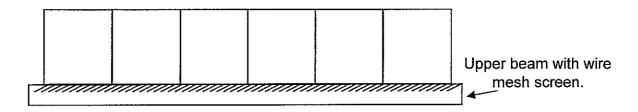
PLAN VIEW OF UPPER SHELF DAMAGE. ~95% consumed. Powder Box remained intact still remains inside - only external minor distorted containers. scorch marks. NO DAMAGE NO DAMAGE ~90% consumed with most 2/15 bottles either missing or bottles distorted. Powder still consumed. 12/15 appear not remains inside distorted affected. ~5 of these 12 have containers. NO DAMAGE scorch marks. Severe scorch marks 1/15 fell into space between front noted on this empty box middle two boxes. facing commodity.

PLAN VIEW OF LOWER SHELF DAMAGE.

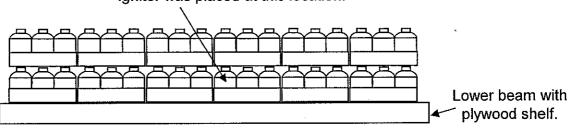
SPRINKLER TEST #9 DAMAGE ASSESSMENT

Commodity: Lower level - Twelve, 1 X 30 pound cartons of calcium hypochlorite product (6 open "hand pick" style at front, and 6 with outer cardboard remaining behind).

> Upper level - Six, 1 X 30 pound cartons of calcium hypochlorite product at the front with outer cardboard remaining and 6 empty boxes behind.



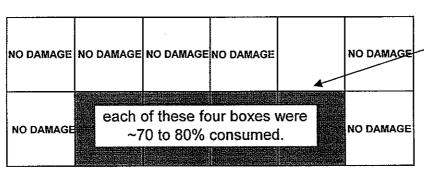
Ignitor was placed at this location.



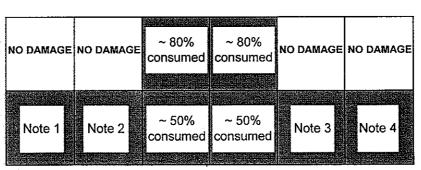
SIDE VIEW OF COMMODITY **ARRANGEMENT**

NOTES:

- Minor scorch marks on caps only. The rest in box were not damaged.
- ~5/12 have scorch marks on top layer.
- 3. ~75% of the bottles have scorch marks. 8/12 on top are intact, with the remainder missing or consumed.
- Scorch marks on bottles closest to "note 3" box.



PLAN VIEW OF UPPER SHELF DAMAGE.



PLAN VIEW OF LOWER SHELF DAMAGE.

Scorch marks only at the face closest to front.

GENERAL NOTES:

- ~25 bottles ended up on the floor and in the aisle.
- Negligible damage to plywood test structure after test.
- Powder C. (product) from the fire was found on the pallet stack across the aisle space.

SPRINKLER TEST #10 DAMAGE ASSESSMENT

Commodity: LOWER TIER:

Eighteen, 1 X 30 pound cartons of calcium

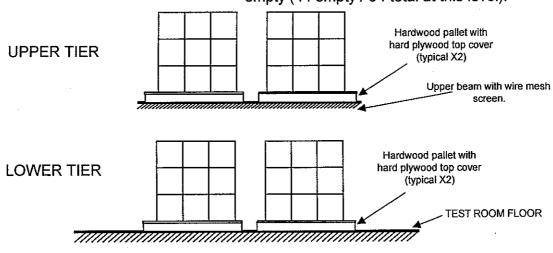
hypochlorite product (9 on each pallet, facing flue). Remainder of boxes were empty (36 empty / 54 total at this level).

UPPER TIER:

Ten, 1 X 30 pound cartons of calcium

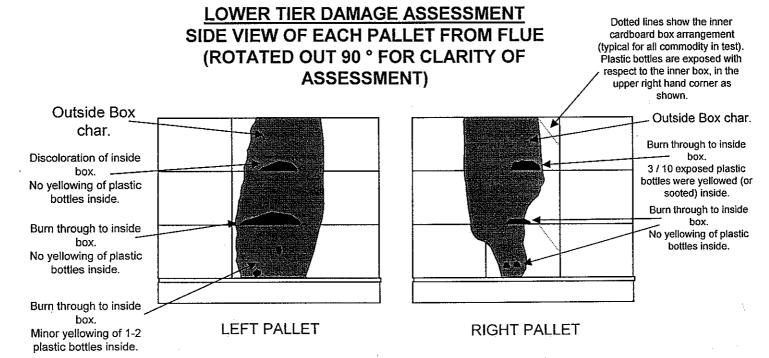
hypochlorite product (5 on each pallet,

facing flue in an inverted "tee" arrangement - 3 high in center). Remainder of boxes were empty (44 empty / 54 total at this level).



NOTE: No damage to upper tier's commodity.

SIDE VIEW OF COMMODITY ARRANGEMENT



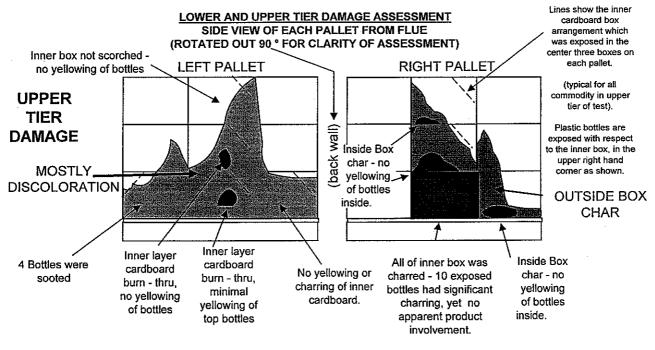
SPRINKLER TEST #11 DAMAGE ASSESSMENT

Commodity:

<u>LOWER TIER</u>: Same arrangement as for test #10, except that the three center boxes on each pallet in the lower tier, closest to the flue had their outer boxes removed to partially expose the plastic bottles inside.

UPPER TIER: Same as for test #10. Surface Charring Consumed Discoloration Hardwood pallet with **UPPER TIER** only hard plywood top cover (typical X2) Upper beam with wire mesh. screen Hardwood pallet with hard plywood top cover LOWER TIER (typical X2) TEST ROOM FLOOR

SIDE VIEW OF COMMODITY ARRANGEMENT - DAMAGE ASSESSMENT



LOWER
TIER ---DAMAGE

18 commodity boxes were ~95% consumed, only powder remained on the floor after the test.

Left pallet - 6 empty boxes to the left of the test enclosure remained standing after the test.

Right pallet - ~4 empty boxes to the back wall and right of the test enclosure remained standing after the test.

The remainder of the empty boxes were strewn about the test room.

SPRINKLER TEST #12 DAMAGE ASSESSMENT

Commodity:

burn thru

commodity

box and-

involvement

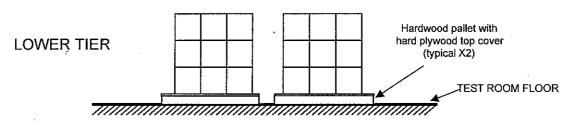
center core of

three - ~80%

consumed

LOWER TIER: Same arrangement as for test #11, (the three center boxes on each pallet in the lower tier, closest to the flue had their outer boxes removed to partially expose the plastic bottles inside). Also, only two additional commodity boxes were used at the bottom of the inner and outer stacks of commodity for a total of 5 boxes of commodity on each pallet (instead of 9 each of the previous two tests). This was designated as an inverted "tee" arrangement.

UPPER TIER: Not used in this test.



SIDE VIEW OF COMMODITY ARRANGEMENT

NOTE: 5 empty boxes were noted in the aisle after the test. A 6th box was ~10' away from the test enclosure.

front face no damage to third group of 9 boxes no damage to third group of 9 boxes Burn thru of empty middle box some charring view looking view looking evident here toward back toward back on outer wall (swung wall (swung column out 90°) of out 90°) of column column closest to closest to wall. wall. BOXE 2nd group of 9 boxes 2nd group of 9 boxes FOR (going from flue to outer wall - no damage (going from flue to outer wall Breach PLANE thru top of empty box - inner box was destroyed apparent breach but Outer box minimal charring commodity involvement consumed center core of **LEFT PALLET RIGHT PALLET** three - ~80% ~80% (view from flue) (view from flue) consumed consumed

burn thru of empty

commodity from

LOWER TIER DAMAGE (As shown from flue)

APPENDIX E

LARGE SCALE CALORIMETRY FIRE TEST PHOTOGRAGHS

Large Scale Calorimetry Fire Test Photograghs

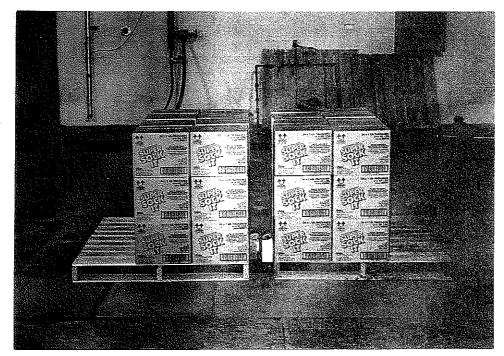


Photo 1 Free-burn Test No. 2 Configuration and Ignition Location

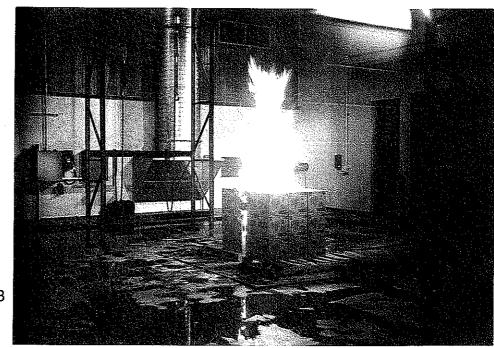


Photo 2
Free-burn Test No. 3
During Test

Large Scale Calorimetry Fire Test Photograghs

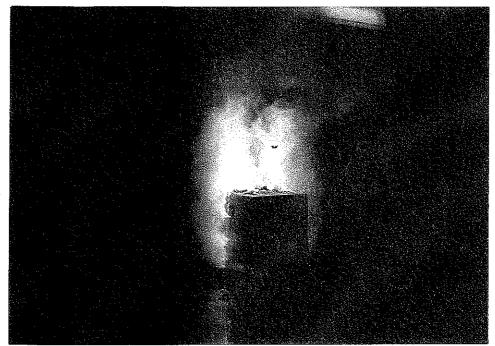


Photo 3
Free-burn Test No. 3
During Test



Photo 4
Free-burn Test No. 3
During Test

Large Scale Calorimetry Fire Test Photograghs



Photo 5
Free-burn Test No. 3
During Test



Photo 6
Free-burn Test No. 2
Post Test

APPENDIX F

SPRINKLERED FIRE TEST PHOTOGRAGHS



Photo 1
Sprinkler Test No. 1
Lower Tier Sprinkler
Locations

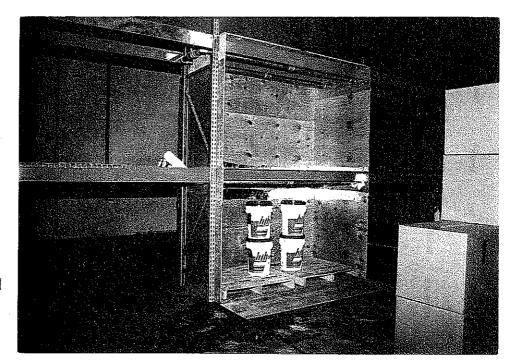


Photo 2 Sprinkler Test No. 1 Configuration

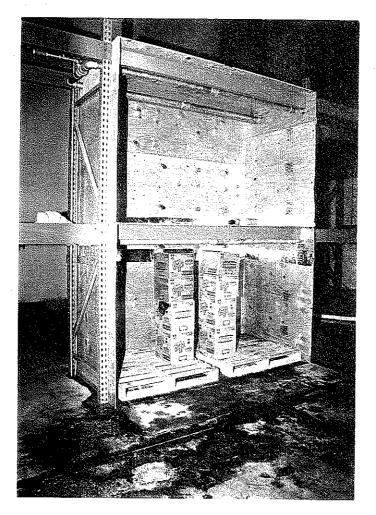


Photo 3
Sprinkler Test No. 3
Configuration



Photo 4
Sprinkler Test No. 4
Close-up of Configuration



Photo 5
Sprinkler Test No. 5
Close-up of Configuration



Photo 6
Sprinkler Test No. 7
Close-up of Configuration

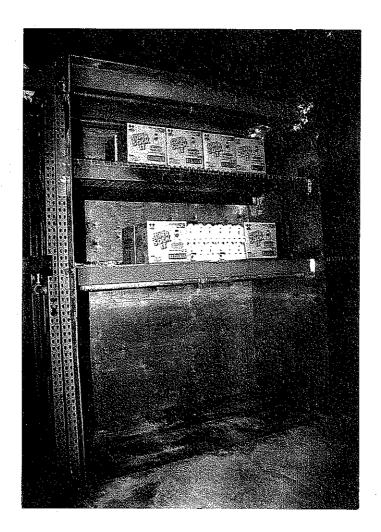


Photo 7 Sprinkler Test No. 8 Configuration

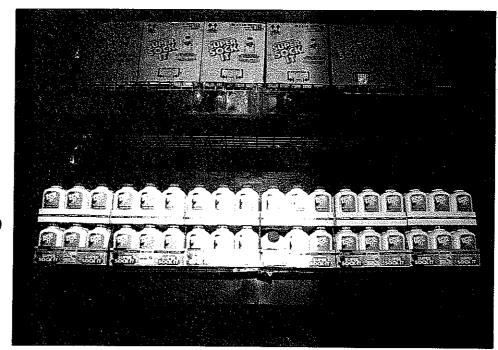


Photo 8
Sprinkler Test No. 9
Close-up of Configuration

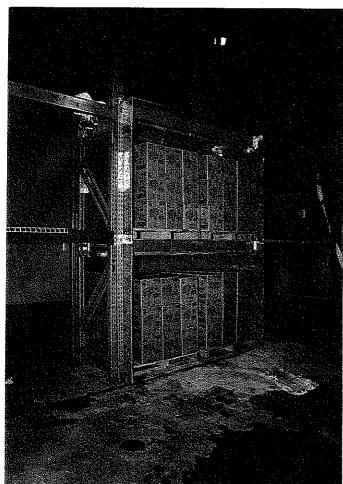
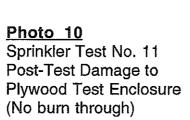


Photo 9
Sprinkler Test No. 10
Configuration



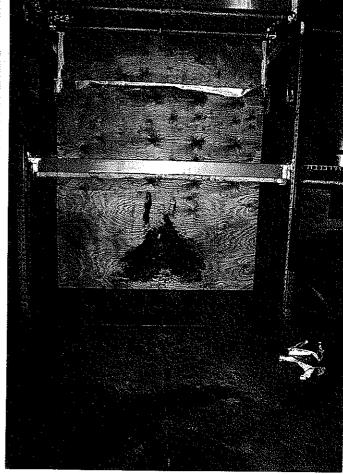
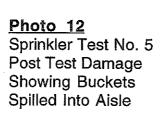




Photo 11
Sprinkler Test No. 1
Post Test Damage
to Lower Bucket



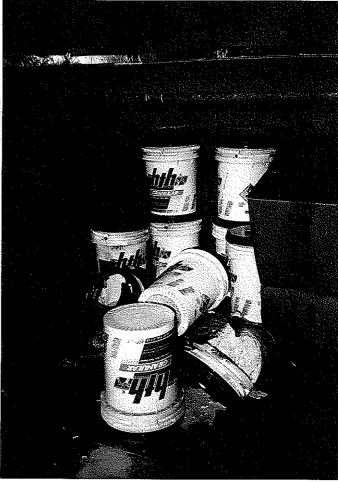




Photo 13
Sprinkler Test No. 10
Post Test Damage To
Outer Cardboard On
Lower Tier

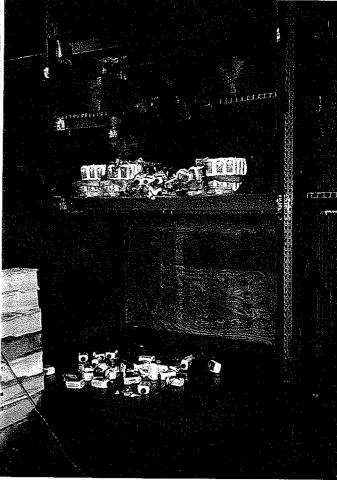
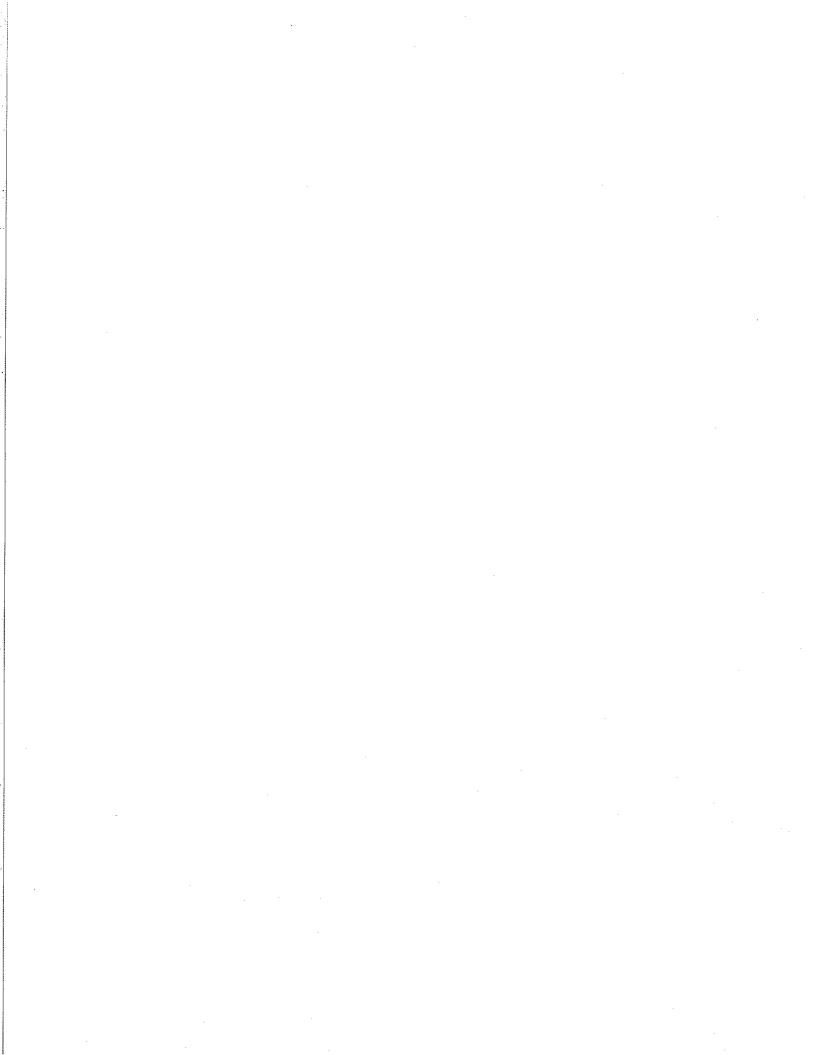


Photo 14
Sprinkler Test No. 9
Post Test Damage
Overview

APPENDIX G

ABSTRACTS



1. Mandell, H. C. Jr., "A New Calcium Hypochlorite and a Discriminatory Test", Fire Technology, pp. 157-161, May 1971

Anhydrous calcium hypochlorite has 2 characteristics that ranks it as one of the most hazardous materials in the average home. These characteristics include its oxidizing power as well as its ability to undergo a self-propagating decomposition reaction.

At a typical 70% concentration, almost the equivalent of 70% "available chlorine", anhydrous calcium hypochlorite is a powerful oxidant. When in contact with fuel substances, it can react producing heat, gases, dust, and flame. This reaction can be spontaneous with liquid fuel substances. Certain solid fuel substances, such as paper and wood, do not readily react with calcium hypochlorite, unless moistened with water, which can act as a reaction medium.

Decomposing calcium hypochlorite produces a considerable amount of oxygen. Therefore, if combustible materials are present and become ignited, they will burn in this oxygen-rich atmosphere with great violence.

The concentration range of calcium hypochlorite as a sanitizer is .1 to 100 ppm in water. As a swimming pool disinfectant, it is typically \leq 1 ppm. Although an effective oxidizer at this concentration, it does not present a fire or reactivity hazard.

Calcium hypochlorite decomposes exothermically at or above 356°F (180°C) producing calcium chloride, oxygen, and heat. This decomposition reaction, if initially involving a small amount of material, can self-propagate through a much larger mass of material. This runaway chain-reaction will accelerate until all of the material has been consumed.

A decomposition reaction can be initiated by a spark, minor flame, contamination, or frictional heat. The decomposition reaction propagates through the mass by transferring heat from particle to particle until a chain-reaction develops.

Understanding this process, Pennwalt developed a "non-propagating" form of granular calcium hypochlorite. This material, having a concentration of 65%, used the trade name of "Sentry."

This additive interrupts the heat transfer process by adding a small amount of a non-descript material that acts as a heat sink. If a decomposition reaction is initiated, this additive makes it difficult to raise the temperature of adjacent calcium hypochlorite particles to its decomposition temperature. The additive has properties that raises the heat capacity and lowers the thermal conductivity of the product.

Using differential scanning calorimetry, the non-propagating form of calcium hypochlorite was shown to still develop an exotherm beginning at 356°F (180°C). However, this material also developed an endotherm at 104°F (40°C). The size of the exotherms and endotherms produced during testing were approximately equal. It was inferred that the endotherm prevented propagation by providing the heat sink. Additional phenomenological testing using initiators consisting of a match flame, a lit cigarette, and .3 ml. of glycerin did not result in a propagating decomposition reaction with the "Sentry" product.

2. Clancey, V. J., "Fire Hazards of Calcium Hypochlorite", Journal of Hazardous Materials, Vol. 1, No. 1, pp. 83-94, September 1975

A series of twelve losses involving fires and explosions on ships had been linked to calcium hypochlorite stored onboard. Japanese product had a higher incidence of losses than product produced in the United States. The nature of the incidents, sources of the calcium hypochlorite,

composition of the calcium hypochlorite, possible impurities from raw material, and possible causes of fires are explored. Additionally, the results of comparative testing on various samples of calcium hypochlorite are presented.

The term "available chlorine" is a misnomer. Calcium hypochlorite has a molecular weight of 142.98. The chlorine component of this molecule would have a molecular weight of 70.9 and would equate to a chlorine concentration of 49.6%.

The so-called "available chlorine" is actually a measure of a materials oxidizing power. The method for determining the "available chlorine" involves reacting calcium hypochlorite with potassium iodide and measuring the amount of iodine that is liberated. This reaction liberates 4 atoms of iodine for every molecule of hypochlorite. Using this method to determine the oxidizing power, the "available chlorine" is double the percentage of actual chlorine present in the molecule. Therefore, pure or 100% concentration calcium hypochlorite, having a chlorine concentration of 49.6% will have an "available chlorine" of 99.2%.

This test is not specific to calcium hypochlorite. Oxidizing materials, such as chlorites and chlorates which can be generated in the manufacturing process, are also capable of releasing iodine by this method.

Impurities introduced into the finished product from raw materials can be a source of unstable material. Calcium hypochlorite is produced from chlorine, calcium carbonate or limestone, and sodium hydroxide. Calcium hypobromite and magnesium hypochlorite can be produced if the chlorine is derived from sea water and the limestone has concentrations of magnesium carbonate, respectively. Sodium hypochlorite can also be a byproduct from using sodium hydroxide in the process. Calcium hypobromite, magnesium hypochlorite and sodium hypochlorite may affect the stability of the finished product.

Several incidents have occurred with intact drums where spontaneous ignition was suspected. Spontaneous ignition can result if unstable species are produced during the manufacturing process or if the product becomes contaminated after manufacturing with an unstable material.

Fires can also be initiated through contact between calcium hypochlorite and organic material. As little as 1 drop of glycerin can initiate a decomposition reaction that can propagate through an entire drum. Liquid fuels or moisture can assist with ignition as it can result in more intimate contact with a contaminant. Certain metal oxides can catalyze a decomposition reaction. Also, ignition or decomposition may not be spontaneous, but may occur later with sensitized material as a result of frictional forces.

At normal temperatures, calcium hypochlorite will decompose and lose approximately 2% of its chlorine annually. Given the slow rate of heat generation, the temperature of the mass will not rise appreciably, particularly with small drums. An uncontrolled decomposition reaction is however more likely to occur in a large drum rather than a small drum. The heat that is generated in the decomposition process will not be transferred to the surroundings as readily as with a large drum. A decomposition temperature of 356°F (180°C) is reported in the literature.

Unlike some oxidizing agents, such as potassium nitrate, the production of oxygen during a decomposition reaction is exothermic. A decomposition process involving calcium hypochlorite can proceed with explosive violence particularly if combustible materials become involved. If combustible materials are involved, the total heat release would include the heat of decomposition plus the heat of combustion.

A research program was initiated to determine why Japanese product had a higher incidence of losses than product produced in the United States. Based upon sample analysis of Japanese and United Stated produced material the following was revealed:

- X-ray diffraction patterns revealed that sodium chloride and up to 4 other unidentified components were present in Japanese product.
- Particle size and density differed with Japanese product and there was greater impact sensitivity with samples with larger particle size.
- Japanese product showed greater differences in reactivity as determined by heat of solution.
- Product produced in the United States decomposed at a steady-state rate, whereas Japanese product decomposed initially at a higher rate and then accelerated to a run-away rate.
- Japanese product showed more variability in properties and behavior than product produced in the United States.

As a result of this analysis, a recommendation was made to store calcium hypochlorite on deck as opposed to below deck. This would allow shipments to continue, thereby mitigating but not preventing the effect of losses, until more research can be performed.

3. Uehara, Y., "Fire and explosion hazards of high strength calcium hypochlorite", Anzen Kogaku, 16 (2), pp. 94-100, 1977

Japanese paper with translation provided in Chemical Abstracts, Vol.91, 1979, 91: 180693p, as follows:

"Fire and explosion hazards of high-strength calcium hypochlorite, Ca(ClO)₂, [which contains about 70% Ca(ClO)₂] were studied. Thermal properties, ignition temperatures, sensitivities for shocks, flame propagation rates, and explosive powers of Ca(ClO)₂ org. materials were measured.

Ca(ClO)₂ decomposes exothermically to release O₂ at 356°F (180°C) and 680°F (360°C). The former decomposition is dominant in fire hazards. But this material does not ignite alone.

Mixtures with combustible substances ignite easily and spread the fire; also, they explode violently from strong shocks."

4. Uehara, Y.; Uematsu, H.; and Saito, Y., "Experimental study of critical thermal ignition temperature of high strength calcium hypochlorite", Anzen Kogaku, 16 (3), pp. 153-158, 1977

Japanese paper with translation provided in Chemical Abstracts, Vol.91, 1979, 91: 159834a, as follows:

"Critical thermal ignition temperatures of high strength $Ca(CIO)_2$ were studied under practical conditions. The extrapolation of the critical ignition temperatures obtained from the small scale experiments to the practical size was examined on the basis of the Frank-Kammenetskii critical ignition theory. Specific heat, thermal conductivity, and heat of reaction of the sample obtained experimentally or thermodynamically were 0.26 cal/g degree, 6.26 x 10^2 cal/cm_min_deg, and 20.8 kcal/mole respectively.

From these data, kinetic parameters on the ignition were calculated as E=29.5 kcal/mole and $A=8.74 \times 10^{13}$ /min. The equation of critical ignition temperature for samples of any size is In T_c + 7422.5 (1/ T_c) - (24.222 + In a)=0, where, T_c is the critical temperature and a is the radius of the sample.

Extrapolation from the equation gave 75.0 °C and 76.3 °C as the ignition temperatures of commercially available containers with diameters of 38.2cm and 35.4 cm, respectively while experiments showed 75 °C and 77 °C, respectively."

5. Uehara, Y.; Uematsu, H.; and Saito, Y., "Spontaneous thermal ignition of high-strength calcium hypochlorite", Presented Paper - 5 th. International Symposium on Transportation of Dangerous Goods on Sea and Inland Waterways, G1, pp. 1-19, 1978

Note: This paper is virtually the same as the Uehara, Y.; Uematsu, H.; and Saito, Y. publication that appeared in Combustion and Flame in the May 1978 issue and is abstracted below.

6. Uehara, Y.; Uematsu, H.; and Saito, Y., "Thermal Ignition of Calcium Hypochlorite", Combustion and Flame, 32, pp. 85-94, May 1978

Small scale experiments were conducted on "high strength" calcium hypochlorite to determine the thermal ignition properties of this material. The apparent activation energy (E) was listed as 29.5 kcal/mole and the frequency factor (A) was listed as 8.74 x 10 ¹³ /min. The critical ignition temperatures were 77 °C and 75 °C for commercial containers of 35.4 cm and 38.2 cm diameters.

The decomposition reaction is shown as:

 $Ca(CIO)_2$ (s) Y $CaCl_2$ (s) + O_2 (g)

The heat of reaction is exothermic (DH= -20.8 kcal/mole).

The results of a computer simulation, based on the thermal ignition theory, was compared to actual results and were in good agreement.

7. Cane, R. F., "Calcium hypochlorite A potentially hazardous product", Chemistry in Australia, Vol. 45, No. 9, pp. 313-314, September 1978

Calcium hypochlorite, at 70% available chlorine, is available as a white granular powder. It is used, in swimming pools and other water treatment applications, as an algaecide and as a bacteriostat. It is also used by the sugar industry as a disinfectant and to also prevent algae growth.

Uncontaminated calcium hypochlorite is a stable material at room temperature. It is a strong oxidizing agent and will also produce hazardous chemical reactions when in contact with various carbon-based materials.

Calcium hypochlorite becomes unstable when wet. This instability is dependent on the extent of moisture and the presence of certain metal impurities. Under conditions of limited water contamination, slow hydrolysis of calcium hypochlorite can decompose producing chlorine monoxide, chlorine, as well as other chlorinated and oxygenated compounds.

Chlorine monoxide is an unstable material capable of explosive decomposition under a variety of conditions including local overheating, exposure to light, and contamination. The decomposition of chlorine monoxide may initiate a further exothermic decomposition reaction involving calcium hypochlorite.

Calcium hypochlorite is also thermally unstable and can decompose above a temperature of 347°F (175°C). This highly exothermic reaction will result in the formation of oxygen and chlorine.

Six case histories of violent decomposition involving calcium hypochlorite are also cited. In all of these examples, the decomposition occurred a brief time after reopening a container of calcium hypochlorite. A number of times, the calcium hypochlorite was ejected from the container and onto nearby people who subsequently received extensive burns on their hands, arms, and face.

Based upon the review of these and other incidents it was concluded that "any form of high strength calcium hypochlorite is potentially dangerous, particularly if it has been stored for a long time." It was further stated that "the stability of calcium hypochlorite varies with water content, usually introduced by humid air." And lastly, "there is always the chance of the generation of chlorine monoxide, once a container had been opened."

The author presents four recommendations for the safe storage and handling of calcium hypochlorite as follows:

- Calcium hypochlorite should be maintained in the "driest possible condition" and should not be transferred in direct sunlight
- A close-fitting lid should be used on containers of calcium hypochlorite and containers should always be kept closed
- Calcium hypochlorite should be segregated from incompatible material, such as organic matter
- Calcium hypochlorite should be dissolved in water; water should not be added to calcium hypochlorite

8. Faust, J. P., Ph.D., "Calcium hypochlorite", Fire Command, p. 29, May 1979

Calcium hypochlorite is described as a strong oxidizer that can cause fires when contaminated with combustible materials or other pool chemicals. Additionally, excessive heat or fire can initiate a vigorous decomposition reaction if temperatures exceed 350 °F (177 °C). Calcium hypochlorite should be stored in a cool, dry location. However, temperatures of short duration as high as 125 °F (52 °C) will not result in fire or explosion.

Cups and measuring devices should be clean, dry, and free of contaminants. When dissolved, water can bring calcium hypochlorite and certain contaminants into intimate contact, resulting in an adverse chemical reaction. However, if calcium hypochlorite comes into contact with just water or humidity, it will only result in the material clumping and losing strength faster than usual. Adding water to calcium hypochlorite will produce some heat but not enough to cause a vigorous decomposition or fire.

If calcium hypochlorite is involved in a fire, it will intensify the effects of the fire. This is due to the oxygen it will liberate. Fire fighting should be done from a distance or from a protected location using large quantities of water. Other fire protection agents, such as carbon dioxide or dry chemical, will not be effective and should not be used. Fire fighters should wear self contained breathing apparatus.

Calcium hypochlorite is noncombustible but can generate large quantities of oxygen if involved in a fire. This could be sufficient to cause an explosion if the pressure is confined. Calcium hypochlorite should be handled in a manner to prevent spills and if spills do occur, they should be flushed with copious quantities of water. Containers should be secured and kept away from children. Calcium hypochlorite should not be transferred to other containers due to the

potential for contamination. Empty containers should be disposed of properly and directions on container labels should be followed.

9. Cane, R. F., "Calcium Hypochlorite - a hazardous substance", Fire Engineers J., pp. 41-42, June 1983

A brief history is given on the development of chlorine-based compounds, used for sterilizing and disinfecting, leading to the eventual production of calcium hypochlorite. A few of the properties of calcium hypochlorite are discussed. Calcium hypochlorite is categorized as an unstable material. When dissolved in water, calcium hypochlorite produces chlorine, oxygen, and hypochlorous acid, all powerful oxidizers and disinfectants.

The term "available chlorine" is explained as being based on an old laboratory method for determining the effectiveness of bleaches. This titration procedure, which uses a solution of potassium iodide, provides a measure of oxidizing power and not the concentration of chlorine. Oxidizing compounds containing no chlorine can be given an available chlorine value based on this method. Pure calcium hypochlorite contains 49.6% chlorine, but has a so called "available chlorine" value of 99.2%. Also, calcium hypochlorite based products, due to the method of calculation, have nearly the same numeric value for "available chlorine" and actual active ingredient in the product.

As of the date of this publication, there were 9 established methods for the production of calcium hypochlorite. During production, minimizing unwanted by-products, including calcium chloride and calcium chlorate, is desirable as their presence can lead to product instability.

Product instability can also result from a number of other conditions. Trace impurities, such as iron, nickel, cobalt, and magnesium, which can be found in lime used as a raw material, can result in an unstable finished product. In the past, calcium hypochlorite produced in Japan was involved in a series of serious loses attributed to decomposition reactions. This product was identified as having a relatively high magnesium hypochlorite concentration.

Calcium hypochlorite is typically produced with a moisture content of less than 1%. If the moisture content of the finished product is between 2% and 10% it can have a pronounced effect of the stability of the material. Also, the rate of decomposition and amount of chlorine and oxygen produced will be significantly higher with a high water content.

A thermally induced decomposition reaction can occur with calcium hypochlorite between a temperature range of 176°F (80°C) and 338°F (170°C). This decomposition reaction can be quite vigorous and the exact temperature at which it will occur is dependent on impurities in the product.

Moisture can be added to a container of calcium hypochlorite if it is left open in humid air. If this occurs, chlorine monoxide can be produced in the container. Chlorine monoxide is more unstable than calcium hypochlorite and can decompose under a variety of conditions. This includes exposure to sunlight, organic matter, and certain metal impurities. A decomposition reaction involving chlorine monoxide can initiate a further decomposition reaction involving calcium hypochlorite.

Certain organic materials, when in contact with calcium hypochlorite, can also result in both decomposition and combustion reactions. These mixtures may react spontaneously or may be initiated by friction or temperature.

In the event that a decomposition reaction does occur, due to the volume of chlorine and oxygen gas produced, calcium hypochlorite can be expelled from its container and propelled onto the

surrounding area. If combustible material is in the surrounding area it can be expected to become involved in a fire. This ensuing fire would be very intense due to the large volume of oxygen present.

A decomposition reaction involving calcium hypochlorite is extremely exothermic. Therefore, if a decomposition process begins it can produce a "hot spot" within the material. If the amount of heat being generated is greater than the heat transfer to the surroundings, the temperature of the entire mass will increase. This process can occur with little warning. I some cases involving metal containers, the first obvious signs were blistering paint on the outside or a red hot container.

A series of publicized losses involving calcium hypochlorite are mentioned. These losses include major fires on ships, fires during repackaging operations, and fires while individuals were handling this material. A number of these incidents resulted in serious injuries and fatalities. The cause of a number of these incidents was surmised to be contamination with organic matter.

Guidance on the safe handling and storage of calcium hypochlorite are offered as follows:

- Store in a cool, dry location using original air-tight metallic containers.
- Open containers in subdued light.
- Use a clean, dry, and dedicated metal scoop or bucket to transfer calcium hypochlorite.
- Do not allow calcium hypochlorite to come into contact with or store near organic material or other pool chemicals.
- Do not drop or roll containers.
- Spilled calcium hypochlorite should not be returned to container. It should however be diluted with copious quantities of water.
- Clothing that has come into contact with calcium hypochlorite should be removed and soaked in water as it may otherwise ignite spontaneously.
- Keep calcium hypochlorite out of reach of children.
- Treat calcium hypochlorite as a hazardous material with unpredictable behavior.
- 10. Anderson, Don, "Hazardous Pool Chemicals", American Fire Journal, Vol. 37, Issue 2, p. 47, February, 1985

Calcium hypochlorite can produce intense fires and explosions if handled improperly. As an oxidizer, it will accelerate fires due to the oxygen that is produced.

Calcium hypochlorite, which is sold as a powder, granules, or tablets, is used to purify swimming pool water. This material is stable under "ordinary conditions" and by itself is considered noncombustible.

When involved in a fire, it can produce lethal levels of chlorine. It is also a strong irritant and can burn the eyes, skin, and mucous membranes. Ingestion of this chemical can be fatal.

Calcium hypochlorite becomes very reactive when wet or mixed with most acids. When in contact with combustible material, especially when wet, the resultant mixture may burst into flames.

Accidents with calcium hypochlorite can be prevented by following the product directions. The material should be kept cool and dry in the original container. Transfers of calcium hypochlorite should be done using clean, dry vessels. Water should never be added to this material. Calcium hypochlorite should be added to water while stirring.

Calcium hypochlorite should be separated from organic material and never mixed with household cleaners, acids, solvents, or other pool chemicals. Gloves should not be worn when handling calcium hypochlorite as they may ignite spontaneously if impregnated.

If the eyes or skin come into contact with calcium hypochlorite, they should be washed with running water for 15 minutes.

11. Clancey, V. J., "Calcium Hypochlorite: A fire and explosion hazard", IChemE Symposium Series No. 102, pp. 11-23, (Exact Date Unknown but after 1986)

Calcium hypochlorite, Ca(OCl)₂, is a powerful oxidizing agent used to sanitize water supplies and swimming pools. The commercial material is a blend containing calcium hypochlorite and varying quantities of different salts. It is produced by chlorinating a lime slurry. The material is primarily manufactured in the United States and Japan and then shipped to other countries in large quantities.

Several years ago there were a series of serious losses involving ships transporting this material. Typically steel drums with plastic liners would be involved in a sudden explosion followed by an intense fire.

The actual oxidizing capacity of calcium hypochlorite is expressed as "available chlorine" which is a misnomer. The percentage of actual chlorine in the molecule is actually half of the nominal "available chlorine". The actual amount of calcium hypochlorite is approximately equal to the nominal "available chlorine". Therefore, a product with 70% "available chlorine" will have an actual concentration of calcium hypochlorite approximately equal to 70% and 30% of other salts. This material will have a percentage of actual chlorine approximately equal to 35%.

An exothermic decomposition reaction can be initiated within a drum of calcium hypochlorite by a single drop of glycerin. Decomposition reactions involving calcium hypochlorite have been attributed to contamination of the material or have occurred in sealed containers spontaneously. There are also instances where the material has been stored without incident.

Bleaching powder, or chloride of lime, has a history of spontaneous decomposition. The decomposition of this material, which can have an "available chlorine" level between 30-35%, has been attributed to contamination by trace amounts of oxides of iron or manganese and possibly calcium chlorate.

Bleaching powder is described as a complex and variable mixture of calcium hypochlorite $(Ca(OCI)_2)$, calcium hydroxide $(Ca(OH)_2)$, calcium chloride $(CaCI_2)$, and water. The "high test" calcium hypochlorite is primarily $(Ca(OCI)_2)$ with various sodium salts and some calcium chlorate.

The commercial grade of calcium hypochlorite loses approximately 2% "available chlorine" per year. This slow decomposition reaction produces chlorine, chlorate, and chlorine monoxide. This reaction is accelerated by the presence of carbon dioxide.

The results of a series of experiments are also discussed. These experiments included the determination of "available chlorine", bulk density, sieve size, species present including various metals, heat of solution, sensitivity to impact, and thermal stability. The results of this analysis revealed a variability in the results of various calcium hypochlorite samples tested.

In conclusion, the incidence of spontaneous decomposition of uncontaminated drummed calcium hypochlorite was categorized as a rare event. The contents of these drums therefore may have contained lower stability, higher sensitivity material. Also, exposure to high ambient

temperatures for a period of time may have initiated decomposition. Some decomposition incidents may have been the result of sensitive decomposition products, such as chlorine monoxide, corrosion products or contamination by foreign material.

12. Custer, Richard L., "Swimming Pool Chemical Plant Fire - Springfield Massachusetts", United States Fire Administration, Federal Emergency Management Agency, Technical Report Series - 027, TriData Corporation, Arlington, VA, 79 p., 1988

On June 17, 1988 rain water entered the building and wet trichloroisocyanuric acid within in a dust collection system. The resultant reaction between water and trichloroisocyanuric acid released chlorine gas and started a fire. This incident was brought under control by covering the trichloroisocyanuric acid with sodium carbonate (soda ash). Later that evening, it rained again and rainwater entered the building through broken windows and onto drums of trichloroisocyanuric acid. This also resulted in a reaction between water and trichloroisocyanuric acid which released more chlorine gas and ignited another larger fire. The partially sprinklered building sustained significant damage and approximately 6000 people had to be evacuated due to the chlorine gas. Reportedly, the fire department was not adequately prepared for the incident. The incident, which lasted 4 days, was finally brought under control by using flooding quantities of water.

As a postscript, this report also refers to another fire having similar circumstances in Glendale, Arizona. This fire occurred on August 21, 1988. The fully sprinklered building was a complete loss and approximately 200-300 people had to be evacuated from the surrounding area. The official cause was listed as undetermined, however, it has been speculated that the cause of the fire was rainwater wetting stored trichloroisocyanuric acid. During the fire heavy red-brown smoke was generated which most likely contained oxides of nitrogen and chlorine.

13. Fire, Frank L.., "Chemical Data Notebook Series # 58: Calcium Hypochlorite", Fire Engineering, pp. 163-167, March 1991

The article, which is written for the fire service, describes calcium hypochlorite, a white crystalline solid having the odor of chlorine, as a material that will not burn itself but will support combustion. This material is a powerful oxidizer and is also corrosive, toxic and an irritant.

Its is used as an algaecide, bactericide, bleaching agent, deodorant, disinfectant, fungicide, oxidizing agent, and water purification agent. The material has a molecular weight of 143 and a specific gravity of 2.35. This material is water soluble but will react with small amounts of water. Calcium hypochlorite can generate oxygen and chlorine which can cause sealed containers to explode.

Adverse chemical reactions, including spontaneous ignition and explosions, both deflagrations and detonations, can occur if calcium hypochlorite comes into contact with certain organic and inorganic material. These reactions can be initiated with a small amount of energy. Calcium hypochlorite can also become unstable if heated. Most homeowners do not understand hazards associated with material.

In terms of toxicity, the threshold-limit value/time-weighted average (TLV/TWA) and the short-term exposure limit (STEL) are 1 ppm and 3 ppm (as chlorine gas), respectively. Depending on the amount ingested, irritation, burns, nausea severe pain, coma, and possibly death could result. Inhalation of calcium hypochlorite can cause damage to respiratory system or be fatal if sufficient quantities were inhaled. Skin and eye contact can cause irritation and burns.

Measures should be taken to prevent releases of calcium hypochlorite as it will present a hazard to living organisms. Releases of calcium hypochlorite into the environment or sewer systems should be reported to the proper authorities, if they occur.

In the event of a fire involving calcium hypochlorite, an exposure fire can result in instability of the material. Chlorine and oxygen can be produced through decomposition. Consideration should also be given to contaminated fire water runoff.

Personal protective equipment (PPE) should be worn to prevent exposure from calcium hypochlorite. PPE should also be compatible for use with calcium hypochlorite. Lastly, some basic first aid advice is presented for inhalation, eye contact, skin contact and ingestion of calcium hypochlorite.

14. Clarke, Patrick K., Szymanski, David J., and Sachen, John B., "Swimming Pool Disinfectants: Seasonal Usage and Storage Hazards; Bellevue Incident; Haz-Mat Toy Store, and Swimming Pool Disinfectants", Fire Engineering, Vol. 145, Issue 7, pp. 73-74, July 1992

Bellevue Incident

The general details of a fire department response at a residence where an explosion occurred were provided. This incident occurred on September 2, 1991 in Bellevue, NE. Reportedly, the homeowner mixed calcium hypochlorite with chlorinated isocyanurates in a swimming pool filter assembly. When water came into contact with these materials, an explosion ensued. The wood pool deck was scorched but did become involved in fire.

Haz-Mat Toy Store

The general details of a fire department response to a fire and haz-mat incident at a toy store were provided. The store which was sprinklered had several types of pool chemicals in the inventory including chlorinated sanitizers and algaecides. When the fire department arrived a number of sprinklers were operating which in conjunction with fire department operations resulted in control of fire. During the incident several fire fighters were overwhelmed by chlorine gas and required medical treatment.

Swimming Pool Disinfectants

Calcium hypochlorite and chlorinated isocyanurates are two common types of swimming pool disinfectants. They are sold in various forms under several brand names. These two chemicals are incompatible with each other as well as other pool chemicals such as algaecides, clarifiers, conditioners, and cleaners.

These disinfectants are dry solids having strong oxidizing properties. They are noncombustible, and stable when free from contamination and stored in a cool, dry, well ventilated area.

Incompatibilities also exist between pool disinfectants and acids, alkalis, organic liquids, peroxides, floor sweepings, and other easily oxidized materials.

Swimming pool disinfectants are also referred to as calhypo, trichlor, dichlor, and iso. Therefore, it is important to refer to an MSDS for proper identification.

These materials are capable of thermal induced decomposition and will produce a dense white toxic smoke. Contamination can lower the decomposition temperature to the point that spontaneous ignition occurs at room temperature.

Extinguishing fires should be done with copious quantities of water. Dry chemical extinguishers should not be used. If a spill occurs, floor sweeping compounds should not be used. Also, the sanitizer should not be put back into original container or allow to come into contact with water. The material should not be placed into a trash container or put into a sewer in an undiluted form.

For any incidents involving pool chemical sanitizers call CHEMTREC. If they come into contact with the eyes or skin, flush immediately with water for 15 minutes. If ingested, immediately drink large quantities of water and do not induce vomiting. If inhaled, immediately move victim to fresh air.

15. Sawyer, Steven F., "Fire Investigation Report - Merchandising Bulk Retail Store Quincy, Massachusetts - May 23, 1995", National Fire Protection Association, Quincy, MA,17 p

On May 23, 1995 a fire occurred at a sprinklered large volume retail center in Quincy, MA. The Quincy Fire Department speculated that motor oil leaked from containers onto "pool chemicals" resulting in their ignition. The fire was contained by 22 sprinklers and fire department hoselines. Fire damage was limited to a few rack structures, the contents within these racks, and the roof structure. There was extensive smoke damage throughout the store resulting in most of the stock being sold for salvage.

At the time of the fire there were 60 employees and 100 customers within the store. An area evacuation was not conducted. Reportedly, there were 60 minor injuries mostly involving firefighters.

16. Isner, Michael S., "Fire Investigation Report - Persulfate Warehouse Tonawanda, New York - August 18, 1995, National Fire Protection Association, Quincy, MA, 26 p

On August 18, 1995 a fire occurred within a sprinklered warehouse that was part of a larger manufacturing facility in Tonawanda, NY. The warehouse was protected by a dry-pipe sprinkler system which was determined to be inadequate for the type of storage at the time of the fire.

The warehouse, which was a total loss, was used for the palletized storage of ammonium persulfate, sodium persulfate, and potassium persulfate. These materials, which are considered Class 1 oxidizers per NFPA 430, were packaged in polyethylene bags, fiber drums and intermediate bulk containers (IBC's). The IBC's were made from woven polypropylene and a polyethylene liner. The fire was reportedly caused by a decomposition reaction involving some "off-spec" ammonium persulfate. The heat of decomposition apparently ignited the combustible IBC and wooden pallets.

There was one fatality resulting from an employee jumping or falling from a second floor office window. Additionally, several employees were injured including three who sustained chemical burns from contaminated run-off. A civilian also sustained chemical burns from contaminated run-off.

17. Isner, Michael S. and Bielen, Richard P., "Fire Investigation Report - Bulk Retail Store Fire Albany, GA - April 16, 1996, National Fire Protection Association, Quincy, MA, 32 p

On April 16, 1996 a fire occurred at a sprinklered large volume retail center in Albany, GA. The fire resulted in a total loss of the facility. The cause of the fire was not determined, however, it began in the area where "pool chemicals" were displayed/stored.

At the time of the fire there were approximately 100 employees and 85 customers within the store. Two people received minor smoke-related injuries.

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