Chapter 4

Self-heating and Thermal Ignition of Calcium hypochlorite

4.1. Introduction

4.1.1. The issue of calcium hypochlorite transport.

Only a limited number of countries manufacture calcium hypochlorite on a commercial scale with Japan, China, India, Egypt and the USA being the main manufacturing nations. Transport is usually by sea with many tens of thousands of tonnes of this material transported annually. Since the late 1960’s, calcium hypochlorite in one form or another has been directly responsible for, or at least linked to, many fires and explosions aboard cargo vessels. The experimental investigation reported in this thesis is in response to several recent fires aboard cargo vessels. In each incident, a commercial form of calcium hypochlorite was contained within a standard 6m length freight container that was itself, packed within the storage locker of a ‘containerised’ cargo vessel. In each incident the major damage occurred near the calcium hypochlorite cargo suggesting that the fire may have originated from this material. Hence, this present study was initiated to determine whether it is scientifically probable that this fire was a result of spontaneous thermal ignition. Figure 4.1.1 shows some of the damage sustained as a result of a fire involving calcium hypochlorite.
Figure 4.1.1.: A view into the partially unloaded storage locker after the fire. The freight container being removed contained a commercial form of calcium hypochlorite.

4.1.2. Scope of this study.

While there have been a number of studies investigating the decomposition of the commercial forms of calcium hypochlorite, the open literature reveals that no other investigation has been undertaken to determine experimentally, or predict theoretically, the critical thermal ignition behaviour of freight container quantities of this material. Additionally, the open literature shows that the thermal ignition behaviour of some commercial forms of calcium hypochlorite have not been rigorously investigated using orthodox thermal ignition methods. This study has been undertaken to address these issues by:

1. Applying conventional thermal ignition theory and experimental methods to investigate in detail the self-heating chemistry of commercially produced hydrated calcium hypochlorite and determine the fundamental thermodynamic and kinetic self-heating constants.

2. Verifying experimentally the model proposed by Gray (2000), that enables the prediction of the critical ignition temperature of freight container quantities of calcium hypochlorite and then using this model to determine the critical ignition temperature of a loaded freight container.
It should be noted that two major outcomes of this study have been a submission to the International Maritime Organisation (IMO) for revision of the safety requirements and transport procedures for the carriage of this material and the experimental verification of the model proposed by Gray (1999).

4.2. History of Calcium Hypochlorite and Bleaching Powder.

C.L Berthollet first demonstrated the strong bleaching properties of hypochlorite compounds in 1785 while later in 1789, in a French town called Javelle, he developed a liquid bleach known as ‘eau de Javelle’ (Edelstein, 1960). This bleach, which also became known as ‘Javelle water’, was initially manufactured by passing chlorine gas through an aqueous solution of ‘potash of lye’ (potassium hydroxide) resulting in a solution of potassium hypochlorite (Sconce, 1962, page 513). The potash of lye was an expensive material and in 1820, Labarraque replaced the potash with soda ash to produce a cheaper bleach that became known as ‘eau de Labarraque’ or ‘Labarraque’s solution’. Initially, only slightly cheaper than eau de Javelle, eau de Labarraque became significantly cheaper around the turn of the 19th century when cheaper caustic soda was manufactured by way of the LeBlanc and the Solvay processes. It is interesting to note that the term ‘Labarraque solution’ is still widely used today in the industrial and medical fields.

In 1799 two Scotsmen; viz Charles Tennant and Charles Macintosh (who also invented the first waterproof cloth) patented a bleach that was significantly cheaper to manufacture than the early Javelle water. This product was patented as ‘chloride of lime’, but it also became known as ‘bleach liquor’ or simply as ‘bleaching powder’ (Sconce, 1962). The manufacturing process involved passing chlorine gas over slaked lime, a process that is principally the same as modern methods of manufacture. This powdered product was easier to transport than Javelle water and quickly became widely used for bleaching in the textile industry. Following the initial patent, the biocidal properties of hypochlorites were identified, resulting in the widespread use of hypochlorite bleach as a sterilising and disinfecting agent (Sconce, 1962). The original bleaching powder primarily consisted of calcium chloride hypochlorite and it wasn’t until 1880, that calcium hypochlorite was manufactured by ‘Chemische Fabrik Gresheim’ (Cane, 1983).
Modern hypochlorite type bleaches have found widespread use both industrially and domestically, primarily for their biocidal properties. Industrial uses have even extended to the sugar industry where it has been utilised as a general disinfectant and for the control of algal growth in open channels (Cane, 1978). Its use as an algaecide in domestic swimming pools, however, remains the dominant use of calcium hypochlorite.

Three forms of hypochlorite bleach are manufactured and transported globally on a commercial scale. Each form has been classified as a strong oxidising agent under the International Maritime Dangerous goods code (IMDG 5.1) and has been issued with an individual and distinguishing United Nations (UN) number by the International Maritime Organisation (IMO). The UN reference number can be used to obtain information regarding the composition of the substance and any special precaution and procedures associated with the transportation and storage of the material. Two of the three forms of calcium hypochlorite bleaching powder are known as ‘High strength Calcium Hypochlorite’ (HCH), while the third form is of a lower strength and is known as ‘chloride of lime’ or ‘Bleaching Powder’ (BP). One of the two HCH forms is called ‘anhydrous’ HCH (UN1748). It is a mixture containing approximately 70% calcium hypochlorite, with the balance consisting of compounds that are residual from the manufacturing process. While this mixture is classified as anhydrous, the United Nations classification allows moisture contents of up to 5.5% on a wet basis. The other type of HCH is called ‘hydrated’ HCH (UN 2880). It is also a mixture and contains approximately 64% calcium hypochlorite, between 5.5 and 10% water and a similar balance of residual manufacturing compounds to that of anhydrous HCH. Bleaching powder (UN 2208) contains between 10% and 39% hypochlorite compounds of which the dominant species is calcium chloride hypochlorite (Sconce, 1962). The moisture content of BP is variable and similar types of residual compounds to anhydrous and hydrated HCH are generally present in the mixture.

Throughout this thesis, the name calcium hypochlorite will refer to the pure chemical Ca(OCl)₂, while the abbreviation HCH will refer to commercial high strength calcium hypochlorite mixtures and BP to the lower strength bleaching powder mixture.
4.3. **Bleaching Powder – not just an oxidising agent.**

The unstable nature of hypochlorite compounds was first documented by A. W Hofmann in 1861. Following the ‘Great Exhibition’ of 1851, he received a 10 litre bottle of ‘chloride of lime’ which, following many years of undisturbed storage on a laboratory shelf, exploded with such intensity that laboratory apparatus and several window-panes were smashed (Hofmann, 1861). More recently, Bibby and Milestone (1984) have measured the decomposition rate of both hydrated and anhydrous HCH and have concluded that decomposition increases as the HCH moisture content increases, with the hydrated form decomposing at a rate of 2 to 5% per year.

Despite the manufacture and transport of many thousands of tonnes of calcium hypochlorite throughout the world annually in each of the above forms, very few studies have been undertaken, or at least published, regarding the self-heating behaviour of calcium hypochlorite. Of these published studies, only one author has used conventional thermal ignition theory, with other authors relying upon Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), isothermal calorimetry or qualitative tests. While these tests can give information regarding specific properties of calcium hypochlorite, only isothermal calorimetry allows the prediction of the decomposition behaviour of commercial quantities of this material. Predictions using isothermal calorimetry data, however, require assumptions regarding the reaction kinetics, the heat loss condition of the individual sample containers and that of the freight container assembly. Hence, predictions based upon isothermal calorimetry data alone, require large scale verification. In the case of HCH, large scale Critical Ambient Temperature (CAT) measurements (see section would be required, ideally undertaken on a complete freight container.

4.4. **Composition, manufacture and chemistry of calcium hypochlorite.**

4.4.1. **Composition of commercial forms of calcium hypochlorite**

Bibby and Milestone (1984) have performed powder X-ray diffraction pattern (XRD) measurements upon fresh HCH that was labelled ‘70% available chlorine’. These measurements revealed that anhydrous Ca(OCl)$_2$ was the dominant hypochlorite compound, while in HCH samples that were
labeled 65% available chlorine', Ca(OCl)_2.3H_2O was the major component. This study did not state the numerical moisture content of the samples examined, however, hypochlorite products labelled '70% available chlorine' are generally of the anhydrous type, while products labelled '65% available chlorine' are usually of the hydrated type. Bibby and Milestone (1984) also found that in some hydrated HCH samples, the dominant species corresponded to 3Ca(OCl)_2.2Ca(OH)_2.2H_2O, which in the manufacturing industry is called the 'dibasic salt' of calcium hypochlorite (Sconce, 1962). All samples examined in the above study, contained significant quantities of NaCl with lesser amounts of Ca(OH)_2, CaCO_3, CaCl_2, NaClO_3, and Ca(ClO_3)_2.

The composition of typical commercial forms of anhydrous and hydrated HCH is shown in table 4.1. The composition of each mixture is dependent upon the raw materials used and the methods of manufacture and as such, the analyses in table 4.1 are indicative only.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Japan\textsuperscript{a} (Toya Soda)</th>
<th>China\textsuperscript{a} (Shanghai Chloralkali)</th>
<th>USA\textsuperscript{a} (PPG)</th>
<th>Japan\textsuperscript{b} (Nippon Soda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN No</td>
<td>2280</td>
<td>2280</td>
<td>2280</td>
<td>1748</td>
</tr>
<tr>
<td>Ca(OCl)_2</td>
<td>73.0</td>
<td>58.9</td>
<td>63.4</td>
<td>72.51</td>
</tr>
<tr>
<td>CaCl_2</td>
<td>4.73</td>
<td>6.70</td>
<td>6.83</td>
<td>2.05</td>
</tr>
<tr>
<td>Ca(ClO_3)_2</td>
<td>1.58</td>
<td>4.58</td>
<td>4.29</td>
<td>0.78</td>
</tr>
<tr>
<td>NaCl</td>
<td>8.04</td>
<td>14.8</td>
<td>14.9</td>
<td>14.18</td>
</tr>
<tr>
<td>H_2O</td>
<td>1.28</td>
<td>5.60</td>
<td>8.45</td>
<td>1.02</td>
</tr>
<tr>
<td>CaCO_3</td>
<td>ND\textsuperscript{c}</td>
<td>ND\textsuperscript{c}</td>
<td>&lt;0.1%</td>
<td>2.15</td>
</tr>
<tr>
<td>Ca(OH)_2</td>
<td>ND\textsuperscript{c}</td>
<td>ND\textsuperscript{c}</td>
<td>&lt;0.1%</td>
<td>4.06</td>
</tr>
<tr>
<td>Other calcium salts</td>
<td>3.01</td>
<td>3.70</td>
<td>3.05</td>
<td>4.14</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Gray, Holleyhead and Halliburton (1999)

\textsuperscript{b} Uehara, (1977)

\textsuperscript{c} not determined
The author of this current work completed the moisture content determination of the PPG sample and this current value, is a correction to the value reported by Gray, Holleyhead and Halliburton (1999). The composition of BP has not been included in table 4.1 due to its variable chemical composition.

4.4.2. Determination of bleaching strength.

The standard method for determining the oxidation strength of chlorine containing bleaches is the American Standard Test Methods Designation: D 2022-89, 1995 (ASTM D 2022-89, 1995). This test was developed over a century ago to compare the oxidation strength of hypochlorite bleaches and involves a simple iodometric redox titration. The standard reports the oxidation strength in a rather unusual and somewhat ambiguous term called the “available chlorine” (Sconce, 1962). This term has been a source of confusion for several authors when it is interpreted in a literal chemical sense rather than by the original definition. Available chlorine was originally defined as the same weight of the gaseous or liquid chlorine required to produce the same action as the compound in question, the hypochlorite ion (Shreve and Brink, 1977). At the time of the inception of this test, however, it was thought that both of the atoms in chlorine were utilised or ‘available’ for bleaching reactions and therefore, chlorine gas (or liquid) was assigned an available chlorine value of 100% (Sconce, 1962). Later, this aspect was found to be incorrect, with only one chlorine atom utilized in the bleaching process, however, the test method was not changed to reflect this error. Hence, if one calculates the ‘available chlorine’ of a bleach using the correct present day chemical understanding, then the value calculated will be half that reported by the standard method. Thus, the present day ambiguity arises when the definition of ‘available chlorine’ is not adhered to.

The percentage available chlorine for a range of common bleaching agents is shown in table 4.2 with the percentage range that is of interest to this current study being highlighted.
Table 4.2 Available chlorine content of bleaching substances*

<table>
<thead>
<tr>
<th>Pure Compounds</th>
<th>Bleaching Agent</th>
<th>Available Chlorine %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂, chlorine</td>
<td></td>
<td>100(^a)</td>
</tr>
<tr>
<td>Ca(OCl)₂, calcium hypochlorite</td>
<td></td>
<td>99.2</td>
</tr>
<tr>
<td>NaOCl, sodium hypochlorite (unstable)</td>
<td></td>
<td>95.2</td>
</tr>
<tr>
<td>LiOCl, lithium hypochlorite</td>
<td></td>
<td>121.6</td>
</tr>
<tr>
<td>Chlorosan 70, “Poolchlor 70,” “Perchloron” (^b)</td>
<td></td>
<td>70 - 74</td>
</tr>
<tr>
<td>“HY CHLOR 65”, “Pitchlor”, “HTH” (^c)</td>
<td></td>
<td>64 - 68</td>
</tr>
</tbody>
</table>

| Commercial Preparations | Bleaching powder/chloride of lime | 35 - 37 |
|                        | “Tropical bleach” \(^d\)          | 25 - 30 |
|                        | “Lo-Bax,” B-K (dairy sanitisers)   | 50 - 55 |
|                        | Liquid bleach \(^e\)               | 12 - 15 |
|                        | Household bleach                   | 3 - 5.5 |
|                        | Bleach liquor (lime bleach liquor) \(^f\) | 3 - 10 |

\(^*\)Referenced from figure 17.1. Sconce, 1962.
\(^a\) by definition
\(^b\) commercial anhydrous calcium hypochlorite.
\(^c\) commercial hydrated calcium hypochlorite.
\(^d\) A stable form of bleaching powder used in hot climates. Prepared by adding CaO to the dry bleaching powder.
\(^e\) Sodium hypochlorite solution used in the paper and textile industry.
\(^f\) Solution of calcium hypochlorite and calcium chloride used for bleaching paper pulp.

4.4.3. Manufacture of bleaching powder and calcium hypochlorite

Calcium hypochlorite is manufactured commercially generally through the chlorination of slaked lime. The chlorination is typically undertaken within inclined rotating cylinders that are equipped with internal blades that lift and shower the lime through a countercurrent flow of chlorine gas. The differences between manufacturing processes can usually be found in the methods used to extract and dry the HCH product. One method of separation involves treating the slurry with NaCl to precipitate the HCH (Shreve and Brink, 1977; Sconce, 1962). A second method involves cooling the caustic soda treated slurry to -12°C whereupon the salt Ca(OCl)₂·NaOCl·NaCl·12H₂O precipitates. The precipitate
is filtered, then added to a second chlorinated slurry of slaked lime and CaCl₂ where the reaction shown below proceeds to produce HCH as a precipitate.

\[ 2[\text{Ca(OCl)}_2 \cdot \text{NaOCl} \cdot 12\text{H}_2\text{O}] + \text{CaCl}_2 + \text{Ca(OCl)}_2 \rightarrow \]

\[ 4\text{Ca(OCl)}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaCl} + 16\text{H}_2\text{O} \]  

[4.1]

4.4.4. Decomposition reactions of HCH

Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) studies suggest that a range of HCH decomposition pathways are possible depending upon the moisture content of the sample (Bibby and Milestone, 1984). It is generally accepted that anhydrous HCH decomposes according to the reaction [4.2] shown below.

\[ \text{Ca(OCl)}_2 \rightarrow \text{CaCl}_2 + \text{O}_2 \]  

[4.2]

Bibby and Milestone (1984) have shown that, while the above reaction generally dominates the decomposition in anhydrous HCH, up to 40% of the original calcium hypochlorite can disproportionate by the reaction 4.3 shown below.

\[ 3\text{Ca(OCl)}_2 \rightarrow \text{Ca(ClO}_3)_2 + 2\text{CaCl}_2 \]  

[4.3]

The evolution of chlorine gas during the decomposition can proceed by at least two mechanisms. One mechanism involves atmospheric carbon dioxide reacting to form calcium carbonate. (Gray, Holleyhead and Halliburton, 1999).

\[ \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{CO}_2 \rightarrow 2\text{CaCO}_3 + 2\text{Cl}_2 \]  

[4.4]
Bibby and Milestone (1984) have shown that a further reaction takes place with evolution of chlorine gas. This reaction is most likely responsible for the large quantities of chlorine evolved at elevated temperatures and for the increased chlorine evolution rate of hydrated HCH at ambient temperatures. The mechanism is suggested to proceed by the reaction:

\[ \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Ca(OH)}_2 + 2\text{Cl}_2 \]  \[4.5\]

Bibby and Milestone (1984) have also shown by isothermal calorimetry that the decomposition rate and hence, the heat release rate, increases as the moisture content of the sample increases. This study also revealed that the decomposition pathway is dependent upon the heating rate during decomposition. During rapidly heated DSC measurements (>15°C/min), it was found that reaction [4.2] dominated decomposition. At moderate heating rates (10°C/min), the disproportionation to chloride and chlorate became significant, while at low heating rates (1°C/min), both reactions [4.2] and [4.3] are the main reactions involved in the decomposition. This study concluded that the decomposition pathway taken was mostly a result of the contact time with water and water vapour in the sample.

It is generally accepted (Mandell, 1971; Clancey, 1975; Cane, 1978, 1984) that anhydrous HCH is a more reactive material and decomposes in a more explosive and violent manner than hydrated HCH. While this is the case following ignition, it is important, here, to differentiate between the properties that contribute to the self-heating hazard and those properties that contribute to a hazard as a result of an ignition incident, e.g., flame or contamination through spillage or container rupture. It is also important to separate the chemical properties that may lead to ignition from those properties that are only important after ignition.

Mandell (1971) has compared the sensitivity of the two forms of HCH to ignition sources with a series of contrived phenomenological tests involving the treatment of HCH with a series of ignition sources which included matches, flames and cigarettes. A reactivity test called the ‘glycerine test’ was also defined, a test which involved the treatment of HCH with a small quantity of glycerine and observing
the outcome. In each test, the anhydrous HCH product decomposed violently, whereas the hydrated product decomposed more gently or not at all in the case of match and cigarette ignition sources. Tests of this type may be useful in evaluating the sensitivity of this material to an ‘ignition incident’, that is, a contamination incident (glycerine test), a flame or heat source incident or the inadvertent extinguishing of matches or cigarettes into the product, however, these tests, are irrelevant when assessing self-heating hazards. Bowes is also of this opinion where, in reference to ad hoc methods for the determination of minimum spontaneous ignition temperatures and auto ignition temperatures, he states ‘Generally speaking, the results obtained by these methods provide useful guidance, but few have the fundamental significance required here.’ (Bowes, 1984, p186)

In contrast to the work of Mandell (1971), the results of Uehara, Uematsu and Yasumasa (1978), Bibby and Milestone (1984) and Cardillo and Nebuloni (1994), clearly show that the self-heating of hydrated HCH occurs at a much lower temperature and at a significantly higher rate than the anhydrous HCH product. Bibby and Milestone (1984) found that XRD patterns of samples of both hydrated and anhydrous HCH stored at 21°C for 2 years over P₂O₅, showed essentially no change. Thus, from a purely self-heating perspective, the anhydrous product, when contained in fully sealed packages, is the more stable product. This is an aspect that tends to be overlooked by the work of Mandell (1971). Therefore, the question that must be asked regarding the real hazards of each substance is:

*Which is the greater hazard during transit, the problem of self-heating or the problem of an ignition incident occurring during loading and unloading?*
4.5. Previous Maritime combustion Incidents involving HCH

4.5.1. Incidents involving anhydrous HCH

Anhydrous calcium hypochlorite was responsible for at least twelve incidents in the late 1960's and early 1970's (Clancey, 1975) and more recently, has been linked to two incidents in the 1990's (Gray, Holleyhead and Halliburton, 1999). Table 4.3 displays the known incidents involving anhydrous calcium hypochlorite from 1967.

Table 4.3: Known incidents involving anhydrous calcium hypochlorite*

<table>
<thead>
<tr>
<th>Date</th>
<th>Vessel</th>
<th>Details of Incident</th>
</tr>
</thead>
<tbody>
<tr>
<td>1967</td>
<td><em>M.V. Thorstream</em></td>
<td>Explosion while loading at Buffalo, New York, USA; four killed</td>
</tr>
<tr>
<td>-</td>
<td><em>M.V. Dynamic Venture</em></td>
<td>Fire in hold; explosion of drum on quay during subsequent discharge</td>
</tr>
<tr>
<td>1969</td>
<td><em>Unnamed</em></td>
<td>Incident while unloading at Sydney; Reported by Government of Australia to I.M.C.O.</td>
</tr>
<tr>
<td>1969</td>
<td><em>Unnamed</em></td>
<td>Fire and explosion while unloading at Brisbane; Reported by Government of Australia to I.M.C.O.</td>
</tr>
<tr>
<td>1970</td>
<td><em>M.V. Griqualand</em></td>
<td>Fire and explosion</td>
</tr>
<tr>
<td>1970</td>
<td><em>M.V. Indura</em></td>
<td>Fire and explosion at Durban, South Africa</td>
</tr>
<tr>
<td>1970</td>
<td><em>M.V. Chevron Transporter</em></td>
<td>Fire whilst on passage from Panama to Vancouver.</td>
</tr>
<tr>
<td>1970</td>
<td><em>M.V Nicolao</em></td>
<td>Fire and explosion during loading at Savannah, Georgia, USA.</td>
</tr>
<tr>
<td>1971</td>
<td><em>M.V Straat Talbot</em></td>
<td>Fire and explosion whilst on passage.</td>
</tr>
<tr>
<td>1972</td>
<td><em>M.V. Catharina Wiards</em></td>
<td>Fire and explosion whilst on passage.</td>
</tr>
<tr>
<td>1973</td>
<td><em>M.V. Opatija</em></td>
<td>Fire and explosion whilst on passage.</td>
</tr>
<tr>
<td>1973</td>
<td><em>M.V. Manolo Everett</em></td>
<td>Explosion whilst loading; six killed</td>
</tr>
<tr>
<td>1991</td>
<td><em>M.V. Recife</em></td>
<td>Fire aboard – product of OLIN/Control Chemicals Pty</td>
</tr>
<tr>
<td>1998</td>
<td><em>Aconcagua</em></td>
<td>Consignment from China exploded whilst on passage</td>
</tr>
</tbody>
</table>

From Clancey, (1975) and Gray, Holleyhead and Halliburton, 1999.
In many incidents it has been the manufacturer's opinion, that contamination of their product was the cause of these incidents (Gray and Holleyhead, 1999). Contamination may have been a factor in incidents where drums have split or failed and the contents mixed with organic substances, however, this would involve a rapid progression to flaming combustion. The fact that many incidents have occurred at sea, with no signs of smoldering or smoke (Clancy, 1975), suggest that the contamination explanation is most unconvincing for many cases. Furthermore, recent incidents have involved the transport of HCH within freight containers, a fact that suggests that contamination is an unlikely explanation. It should also be noted that prior to the 1980's, the use of freight containers was not widespread and individual drums were manually loaded.

4.5.2. Incidents involving hydrated HCH and Bleaching powder

Hydrated HCH was involved in two maritime incidents in the 1990's, the Contship France and the DG Harmony. The Contship France contained four freight containers of hydrated HCH with two of these freight containers packed with 80 x 193kg drums and two freight containers packed with $480 \times 40$kg drums. Table 4.4 displays the more recent incidents involving hydrated HCH and bleaching powder.

<table>
<thead>
<tr>
<th>Date</th>
<th>Vessel</th>
<th>Details of Incident</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td><em>Tiger Wave</em></td>
<td>Originated from India; UN2208</td>
</tr>
<tr>
<td>1997</td>
<td><em>Contship France</em></td>
<td>Originated from the USA: UN2880</td>
</tr>
<tr>
<td>1998</td>
<td><em>Maersk Mombasa</em></td>
<td>Originated from the Egypt: UN2208</td>
</tr>
<tr>
<td>1998</td>
<td><em>Sea Express</em></td>
<td>Originated from the China: UN2208</td>
</tr>
<tr>
<td>1998</td>
<td><em>DG Harmony</em></td>
<td>Originated from the USA: UN2880</td>
</tr>
<tr>
<td>1999</td>
<td><em>CMA Djakarta</em></td>
<td>Originated from the China: UN2208</td>
</tr>
</tbody>
</table>

*From and Gray, Holleyhead and Halliburton, 1999.
For a number of these incidents, it was the opinion of the manufacturers that incorrect storage was the likely origin of the fire (Gray and Holleyhead, 1999). Given the very limited scientific data available regarding the self-heating properties of all three types of bleaching powder and the number of incidents that has occurred recently, it is clear that a detailed study is required into not only the self-heating properties of hydrated HCH, but also anhydrous HCH and bleaching powder.

4.6. Methods used to estimate the Critical Ignition Temperature of reactive substances.

4.6.1. The traditional method for the determination of the ‘safe’ transport temperature of reactive substances, the SADT test.

Historically, international and national transport regulators (Transport Canada (1997); United States Department of Transport, 1998: section. 173.21; IMO ‘Orange Book’) have used the United States self-accelerating decomposition temperature test (SADT test) to determine the special transport and storage conditions of reactive substances. This test is also used by these organisations to determine the types of cargo ‘forbidden’ for transport or must be transported under temperature controlled conditions (United States Department of Transport, 1998: section. 173.21). The procedure involves the determination of a single temperature, the Self-Accelerating Decomposition Temperature (SADT), which is defined as ‘the minimum constant temperature air environment at which auto-accelerative decomposition occurs for a substance in a specific package’ (UN, 1975: 28.4.1). Clearly, when applied to the Stevedoring industry, the SADT is the maximum temperature at which the reactive substance could be safely transported or stored.

The SADT test is completed within a temperature controlled chamber that is: (UN, 1975: 28.4.1.2.3)

- Well insulated;
- Thermostatically controlled to maintain a uniform air temperature within ± 2°C of the test temperature; and
- The minimum separation distance from the package to the wall is 100mm.
The sample must be in the packaged form intended for commercial use (UN, 1975: 28.4.1.2.1). The weighed sample is instrumented with a thermocouple placed at the centre of the sample. The sample is placed within the chamber and allowed to heat to within 2°C of the of the test chamber temperature. Monitoring of the sample temperature is continued for a further seven days or until the sample temperature rises to 6°C above the chamber temperature. The SADT is defined as the lowest chamber temperature at which the sample temperature exceeds the chamber temperature by 6°C or more (UN, 1975: 28.4.1.3). Further details relating to the experimental procedure used for the SADT tests completed in this study is given in section 5.4.

4.6.2. The critical Ambient Temperature Test

The scientifically accepted experimental procedure used to determine the minimum temperature for self-ignition at constant uniform ambient temperature of a body, defined as the critical ambient temperature (CAT), has been discussed in detail in Bowes (1984, page 471). The detailed description of the experimental procedures involved in this determination is given in section 5.4. The experimental procedure is generally similar to the experimental procedure used to determine the SADT except that the temperature and time constraints are not applied. Briefly, successive test samples of fixed size and geometry are exposed to different temperatures within a temperature controlled oven and allowed to either thermally ignite or fail to ignite. The CAT is obtained through a process of ‘bracketing’. Successive measurements are completed with each measurement increasing the precision between which thermal ignition occurs or fails to occur. In this experiment, the CAT is reported as the arithmetic mean between the lowest temperature at which thermal ignition occurs and the highest temperature at which thermal ignition fails to occur. It is important to report the uncertainty of this determination, which is usually reported as half of the difference between the two bracketing temperatures. (see also page 13)

Throughout this study, the SADT (described in section 4.6.1 page 118) will refer to the temperature reported by the SADT test, the CAT (described in section 4.6.2 page 119) will refer to the temperature determined by the CAT test and the critical ignition temperature (CIT) will refer to the theoretical critical temperature above which stable behaviour is not possible and the body is considered super-
critical (see section 1.2.1, page 7). The latter two definitions are used in this thesis to distinguish the experimentally determined ignition temperature (CAT), which is an experimental approximation of the theoretical ignition temperature (CAT). This distinction is used in the latter chapters of this thesis experimental results are compared to theory.

4.7. Previous studies involving the self-heating of anhydrous calcium hypochlorite

The first published work investigating the spontaneous combustion hazard of anhydrous HCH was by V.J. Clancey (1975) who concluded that there was a significant potential risk of spontaneous combustion in anhydrous HCH during transport. Only limited attention was devoted to hydrated HCH, with researchers concluding that the decomposition of hydrated HCH was less violent than the anhydrous form. It was found that in the absence of combustible materials, the runaway reaction from the decomposition of hydrated HCH in an open topped container did not cause a fire or explosion. V.J Clancey (1975) concluded that a rigorous scientific investigation was required to accurately quantify the self-heating behaviour of this material and that the shipping codes for the transport of the anhydrous material should be revised.

Uehara, Uematsu and Yasumasa (1978) completed the first experimental investigation into the self-heating properties of HCH, using the principles of thermal explosion theory. In this study, anhydrous HCH was investigated using CAT tests ranging in size up to 38.2 cm diameter containers. DSC and TGA measurements were also completed. The CAT tests up to 15.2 cm diameter were undertaken using the normal CAT test procedures except that the samples were contained within a polyethylene pouch which itself was contained within a steel can. During these tests, the explosive behaviour of anhydrous HCH was displayed with the lids of cans being blown off, contents scattered violently throughout the oven and the polyethylene pouch igniting.

An unusual heating method involving steam was used during the experiments on commercial sized containers. The aim of this method was to simulate the heating conditions of humid tropical environments, however, as has been noted by Gray, Holleyhead and Halliburton (1999), the effect of
the steam environment upon the heat transfer coefficient of the HDPE container, is difficult to predict. This is especially the case since control tests, without steam heating, were not undertaken. The CAT's for the commercial containers were 77°C and 75°C for the 35.4cm and 38.2cm diameter containers respectively agreeing closely with predicted temperatures using a Frank-Kamenetskii (1969) extrapolation to these sizes. The authors calculated an apparent activation energy of 123.4kJmol⁻¹ and an Arrhenius pre-exponential number of 8.74 min⁻¹. The raw data from this study are shown in figure 4.5.1 in the form of the Frank-Kamenetskii (1969) plot of \( \ln(\delta_{ct} T_a^2/r^2) \) and 1000/Tₐ.

![Graph showing the Frank-Kamenetskii plot](image)

**Figure 4.5.1: Frank-Kamenetskii (1969) plot of the results from the study by Uehara, Uematsu and Yasumasa (1978). The radius of the test containers were measured in mm and temperature measured in Kelvin.**

The value of \( \delta_{ct} \approx 2.0 \) was used for the Frank-Kamenetskii (1969) calculation in the above figure, a value consistent with infinite cylinder type geometry with an infinite Biot number. This study showed good agreements with Frank-Kamenetskii (1969) theory and suggested that a single chemical reaction
regime is operating. These data have been used by Bowes (1984, page 465) to estimate the CIT of this material for cubes up to 4.3 m. The estimates are shown in table 4.5.

Table 4.5. Estimates of Critical Ignition Temperatures for various sized cubes of hydrated HCH*

<table>
<thead>
<tr>
<th>Ambient temperature (°C)</th>
<th>Critical size (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>40</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* From Bowes (1983) table 10.7

Bowes (1983, page 465) has further suggested that the estimates in the above table ‘are sufficient to indicate a possibility of self-heating and thermal explosion in ‘high-strength’ calcium hypochlorite in warm surroundings such as the upper holds of ships in tropical waters.’

The high-strength’ calcium hypochlorite refered to by Bowes is the anhydrous HCH type.

An incorrect aspect of the interpretation, which has been documented by Gray, Holleyhead and Halliburton (1999), is that a value for \( \delta_c \) for an infinitely long cylinder with a large Biot number (\( \delta_c = 2.0 \)) has been used in the Frank-Kamenetskii (1969) analysis. Given that the geometry of the test container is closer to equicylinder geometry, a more appropriate value for \( \delta_c \) would be 2.5 or 2.6. Also, during CAT experiments, a temperature rise of 6 °C was observed at the outer surface of the container, an aspect clearly inconsistent with infinite Biot number and suggesting that a correction for finite Biot number is appropriate. A third unfortunate aspect is the powdering of anhydrous HCH for conductivity measurements rather than testing this material in its original form. By using finely ground and powdered anhydrous HCH rather than the original granular material, it would be expected that a significantly higher thermal conductivity would be measured compared to its original bulk state. Given the weaknesses in the experimental methods and analysis, the calculated thermodynamic parameters must be considered questionable.
Unpublished critical tests undertaken by ‘Olin’, now ‘Arch chemicals’, (located in the USA) on 45kg samples of hydrated HCH, showed that a 45kg sample survived three weeks at 50°C without incident (Wojtowicz, 1987) while at 57°C the sample was super-critical (Schrodinger, 1979). This temperature is nearly 20°C lower than the CAT of anhydrous HCH (Uehara, Uematsu and Yasumasa, 1978) and clearly shows that the CIT is lowered (for a given sample size) due to the extra water. Tests, undertaken by Safety Consulting Engineers Inc, Illinois, using hydrated HCH again manufactured by Olin, showed that a runaway reaction on 10kg samples occurred at 64°C after 13hrs and 50kg samples after 20 minutes at the same temperature (Dahn, 1979). A number of unpublished “Warmestaulagerung tests” have been completed in the United Kingdom and the results are shown in table 4.5 (Gray, Holleyhead, and Halliburton, 1999).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oven Temperature</th>
<th>Result</th>
<th>Time after reaching oven temperature</th>
<th>Maximum Temperature attained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olin (65% Cl₂, 6.9% H₂O)*</td>
<td>60°C</td>
<td>runaway</td>
<td>19 ½ h</td>
<td>170°C</td>
</tr>
<tr>
<td>Olin (65% Cl₂, 6.9% H₂O)*</td>
<td>60°C</td>
<td>runaway</td>
<td>21h</td>
<td>162°C</td>
</tr>
<tr>
<td>Olin (65% Cl₂, 6.9% H₂O)*</td>
<td>70°C</td>
<td>runaway</td>
<td>7h</td>
<td>174°C</td>
</tr>
<tr>
<td>Olin (65% Cl₂, 6.9% H₂O)*</td>
<td>70°C</td>
<td>runaway</td>
<td>77h</td>
<td>185°C</td>
</tr>
<tr>
<td>Japan (70% Cl₂)*</td>
<td>60°C</td>
<td>No runaway</td>
<td>60h</td>
<td>62°C</td>
</tr>
<tr>
<td>Japan (70% Cl₂)*</td>
<td>60°C</td>
<td>No runaway</td>
<td>60h</td>
<td>70°C</td>
</tr>
</tbody>
</table>

*Cl₂ measured as available chlorine, (ASTM D 2022-89, 1995).

This test involves the heating of small test samples (400g) in a ‘Dewar’ flask at constant temperature to determine the temperature at which a runaway reaction occurs. The results in table 4.5 illustrate the lower critical temperature of the hydrated HCH compared to the anhydrous form from Japan.
The most recent investigation into the self-heating of hydrated HCH is that of Gray and Halliburton (2000), part of which is the subject of this thesis and will be discussed in the following chapters. The work not directly undertaken by the author of this thesis will be identified where appropriate.

Gray (reported in Gray and Halliburton, 2000) examined the self-heating behaviour of both Japanese and American hydrate HCH by conventional CAT tests up to a mass of 10kg. These data suggest the existence of at least two separate reaction mechanisms; a higher temperature reaction that dominates the decomposition chemistry above about 110°C and a low temperature reaction, which dominates the chemistry below this temperature. The results of this investigation are shown in figure 4.5.1.

![Graph showing relationship between $T_a$ and $2\ln(T_{a,cr}/T)$](image)

**Figure 4.5.2: Hydrated HCH CAT completed by Gray. Tests up to quantities of 10 kg were performed in stainless steel gauze baskets.**

Both regions show agreement with the standard Frank-Kamenetskii (1969) model within the temperature range specified. Least squares fitting over the higher temperature range region, suggest an apparent activation energy of $158 \pm 15$kJmol$^{-1}$ (Gray and Halliburton, 2000) for this reaction. The
second mechanism is shown by the linear region extending from about 140°C down to at about 87°C. In figure 4.5.1, this region displays a reduced slope and corresponds to lower apparent activation energy for this mechanism. This is the region, which corresponds to larger size containers that are normally transported and is hence, the region of most interest to this study. The star on figure 4.5.1 indicates this region of interest if it is assumed that no other reactions are significant over the extrapolated temperature range. Clearly, significant uncertainty exists when these available experimental data are used to predict the CAT’s of commercial 40 and 200kg quantities of hydrated HCH. Given the uncertainty in the above extrapolation to commercial quantities and the possibility of other reaction mechanisms existing at lower temperatures, it is clear that larger scale experiments are warranted.

Consequently, after consideration of the limited experimental data available regarding the self-heating of hydrated HCH and hence, little data describing the ‘safe’ transport conditions of this material, the objectives of this study are:

1. to provide accurate experimental kinetic and thermodynamic parameters that will allow the accurate prediction of the thermal ignition hazard of freight container quantities of hydrated HCH,
2. to provide experimental data that describes the behaviour of drums of hydrated HCH when large numbers of these drums are packed into a confined space of limited heat capacity.
Chapter 5

Experimental Methods and procedures used for the Critical ambient temperature measurements of Calcium Hypochlorite

5.1. General safety considerations for undertaking CAT measurements on commercial quantities of HCH.

The experience gained from small scale CAT measurements suggested that copious quantities of chlorine gas would be evolved during CAT measurements involving 40kg and 200kg quantities of hydrated HCH. This toxicity problem, combined with the potential explosion risk (Clancey 1975), suggested that the Macquarie University Combustion Laboratory would be unsuitable for CAT measurements larger than about 10kg. Hence, experiments upon 40kg and 200kg commercial drums of hydrated HCH were undertaken at a remote and isolated site approximately 350km from Sydney.

5.2. Origin of the hydrated calcium hypochlorite sample.

The hydrated HCH used in all measurements was the product of a U.S manufacturer (PPG). The samples were purchased either from a local commercial outlet in Sydney or directly from an importer in Fremantle Western Australia. The sample used during the first experimental series, involving 40kg and 36kg CAT measurements in a forced convection airflow, was purchased from the Fremantle supplier. For the 40kg and 200kg 'still air' CAT measurements, the hydrated HCH was purchased from both the Fremantle supplier and a local Sydney outlet, with each merchant supplying approximately half of the total quantity. The third batch, which was used to investigate interactive effects of self-heating bodies, was purchased from the local Sydney outlet. The quantity of hydrated HCH purchased on each occasion was sufficient to complete a six-month experimental campaign, thereby minimising the impact of decomposition during storage, whilst maintaining a uniform sample during each experimental series. Each 40kg HDPE hydrated HCH sample arrived in an unopened condition displaying the manufacturers label and the unbroken metal seal. The samples were stored at
Macquarie University in a cool dry commercial storage room designed for the storage of oxidising material. The samples were stored at a maximum ambient temperature of ~21°C.

5.3. Apparatus

5.3.1. Apparatus for the 40kg and 36kg CAT measurements in forced airflow.

The first series of 40kg CAT measurements were undertaken using a forced airflow laboratory oven of 150 litres capacity. This oven had been previously modified, with increased baffling, to reduce the maximum internal spatial temperature difference within the oven to less than ± 1.5°C. The original oven door was removed and replaced with a transparent acrylic sheet (Hsinhwa Chemical CO., LTD. 'BEAUTY GLASS') that enabled the continuous observation of the sample throughout the experiment. Glass fibre was packed around the perimeter of the transparent sheet to eliminate air leakage between the edge of the acrylic sheet and the oven. The oven and temperature controller unit were housed within a small open shed located approximately 30 metres from a larger shed that housed the data recording instruments.

During the first 40kg CAT measurements, the high-density polyethylene (HDPE) drum ignited and destroyed the temperature controller unit, the oven fan and motor and also significantly damaged the oven structure. Furthermore, the results from this measurement revealed that the cooling capacity of the oven, in its standard form, was insufficient for these sized measurements resulting in an uncontrolled oven temperature increase towards the latter period of the super-critical measurement. Following this fire and due to the unavailability of a larger capacity replacement oven, the original oven was repaired and modified to improve its thermal performance. While improved stability could be obtained by increasing the air leakage rate from the oven, it was found that the significant increase in heat required to maintain thermal stability resulted in an unacceptably high spatial temperature gradient within the oven. A novel design was eventually developed to improve the thermal stability of the oven without a sacrifice in thermal homogeneity. The apparatus is displayed in fig 5.3.1.
Figure 5.3.1: Schematic diagram of the apparatus that incorporated a ballast drum to increase the total thermal capacity of the oven.

The modification involved connecting a separate 200 litre steel drum to the original oven, thereby, more than doubling the total air volume of the oven in its original form. Two 120mm steel tubes were used to connect the oven to the ballast drum as shown in figure 5.3.1. Within each tube, axial fans were installed and were used to control the air circulation rate between the two units. The heater elements were housed within the 200L drum and all exposed surfaces were externally lagged in glass fibre to a depth of 100mm. Located in the top of the ballast vessel were two openings that were
equipped with removable caps (50mm and 20mm) that allowed the manual regulation of the venting rate of contaminated air. By varying the aperture of the ventilation openings and by controlling the thickness of the thermal lagging, the heat loss could be varied. During super-critical measurements, the heat loss from the oven/ballast combination could be further increased by placing a small fan over the larger opening and forcing a flow of cool air into the ballast vessel. The flow rate of cool air was varied according to the duty cycle of the temperature controller, thereby, resulting in a constant air temperature within the oven at all times. While the dilution of the contaminated air reduced the build up of chlorine gas within the apparatus, the production of copious volumes of chlorine gas by the sample continued to be a significant operational problem. This aspect precipitated the seizure of the axial circulation fans at the conclusion of nearly every experiment and the general failure of electrical connections. All metal surfaces suffered substantial corrosion and the apparatus was unusable after six experiments.

5.3.2. Temperature control and data recording instrumentation during the first experimental series.

A “CAL controls #3200” temperature controller with a precision of ± 0.1°C was used during initial experiments. This temperature controller utilised proportional, integral and differential (PID) control functions as well as “fuzzy” logic to enable rapid heating to the preset temperature with virtually no thermal overshoot. This unit was generally capable of maintaining a constant temperature to within ± 0.25°C of the preset temperature for an indefinite period. Five Chromel-alumel thermocouples were placed within the oven at strategic positions to act as sensors for the temperature controller. These thermojunctions were connected in parallel and reflected the mean ambient temperature within the oven. To quantify the thermal gradients during each measurement, separate chromel-alumel thermocouples were placed at spatially separated positions within the oven and electrical output from each thermojunction manually recorded. The temperature variation between an individual thermocouple and the thermocouple array was less than 0.6°C.
The temperature of the sample centre and the average oven air temperature were recorded continuously on an analogue chart recorder and digitally, at one-minute intervals, with an electronic data recorder (DataTaker® DT50) and computer. Each channel of the chart recorder was individually referenced to the ice point of water (Kaye Instruments – Icepoint/reference model K140-4). The DataTaker® recorded the temperatures of the four thermocouples instrumented within the HDPE drum as well as the mean oven air temperature. The DataTaker® was equipped with internal cold junction compensation and thermocouple linearisation algorithms enabling this unit to record temperature data directly. Other thermocouples were periodically measured with a handheld digital thermometer (Comark KM45) and manually recorded. The handheld thermometer and all thermocouples were calibrated as outlined in section 5.5. When required, a video camera and recorder were used to record the experiments through the transparent oven door.

5.3.3. Apparatus for CAT measurements of 40 and 200kg standing in still air

At the conclusion of the 40kg and 36kg forced convection CAT measurements, a purpose built measurement facility was constructed to safely complete the CAT measurements in excess of 200kg.

5.3.3.1. Oven construction.

This oven was fabricated from kiln fired concrete “besser” bricks to internal dimensions of 1.8m × 1.2m × 1.8m and is shown in a partial state of completion in Figure 5.3.2.
Figure 5.3.2: This figure shows the oven in a state of partial completion. The figure on the left shows the ventilation fan installed.

Figure 5.3.3 shows an internal view of the oven while figure 5.3.4 shows a view of the fan drive assembly.
Figure 5.3.3: The completed oven (shown with the door open). The 600mm circulation fan is shown.

Heater elements (not shown) were placed in front of the fan unit.
The beaker bricks were supported by two fabricated steel frames (50mm x 50mm x 3mm Rectangular Hollow Section (RHS)) and 32 joining "strainer" bars (25mm x 25mm x 2mm RHS) that passed between the end frames and through the bricks. As can be seen in figure 5.3.1, one end of the joining bar was welded to one end frame while the other end was attached to the second end frame using a threaded rod and nut arrangement. During final assembly, the nuts tensioned the bricks between the two end frames producing a rigid shatter resistant structure. The rear wall of the oven was fabricated in a similar manner. To reduce heat loss, the hollow air cavity of each brick was filled with glass insulating fibre. All internal walls of the oven were further lined with a fire retardant paneling. The door consisted of a lightweight, 150mm thick, fabricated steel tubular frame (25mm x 25mm x 2 mm
RHS) lined on all exterior surfaces with a fire retardant board. The frame was side hinged and the internal cavity of the door was filled with glass fibre. Glass fibre was also used to seal the perimeter of the door. In the event of an explosion within the oven, the door was designed to blow out, thus leaving the main structure undamaged.

An externally driven circulation fan (blade diameter of 600mm, rotational speed of 900rpm with an air velocity of 4m/s at a distance of 30cm) was located towards the rear of the oven. The fan drive shaft penetrated through the rear wall cavity through a custom fabricated, 100mm-diameter glass fibre packed tube. The fan was powered by a 0.4kW AC induction motor. In front of the circulating fan were located a bank of air heating elements (6 × 850 Watts). These units were of a finned design that minimised the surface temperature rise of the element and hence, minimised radiative heating.

Following the 200kg measurements, the oven was further modified to comply with the SADT oven requirements. The modification involved moving the heater units and a circulation fan to the outside of the oven. In this configuration, air was drawn through a 300mm penetration located at the top corner of the rear wall of the oven, along a 300mm steel duct into a 1.2kW centrifugal fan. Both the duct and the fan housing were insulated to a thickness of 200mm with glass fibre. The air was discharged into an enclosed conduit, constructed from 'Hebel' (manufactured by CSR building products Australia) fire rated blocks. The airflow was directed over the heater elements and finally, discharged into the lower rear corner of the oven. Figures 5.3.5 to figures 5.3.8 show the modified flow ducting and housing in various stages of completion.
Figure 5.3.5: View of the rear of the oven showing the heater housing. The motor and driveshaft for the 600mm fan can be seen in the foreground. Part of the heater unit can be seen through the slot located to the right of the electric motor. Multiple high temperature cables can be seen exiting the housing. Oven air is forced into the slot to the right of the motor and over the heater elements before entering the oven.

Figure 5.3.6: View of the rear of the oven showing the heater housing and ducting. The motor and drive shaft for the 600mm fan and the heater cabling are again visible. The 300mm diameter ducting that connects the wall penetration located at the top rear of the oven to the circulation fan (shown in the figure below) can be seen towards the lower left of the figure. The brick ductwork connecting the circulation fan to the heater housing is now complete and can be seen towards the right of the motor.
Figure 5.3.7: (left) and Figure 5.3.8 (right): View of the exterior rear of the oven showing air circulation fan and ducting. The 300mm diameter ducting that connects the penetration located at the top rear of the oven, to the circulation fan can be seen insulated with a layer of glass fibre (left) and with an additional layer of silver 'ANTICON BLANKET®'(right). The brick ductwork connecting the circulation fan to the heater housing can be seen towards the right of the fan housing.

An 80mm diameter clean air inlet duct was located at floor level behind the circulation fan. A 120mm diameter exhaust duct was also located near the top of the oven, but diagonally opposite the inlet duct. The inlet duct also served as a path for the entry of the heater power cables. Chlorine gas contaminated air was exhausted through a 120mm polyvinylchloride (PVC) tube that discharged approximately 50m away from the oven. A ‘bilge blower’ was initially installed into the PVC tube to extract the contaminated air, however, while this unit was designed for corrosive marine environments, it
generally failed at the conclusion of each run. Eventually, a custom manufactured air mover was installed. This unit incorporated a sealed motor that was separated from, but coupled to, the fan housing. This final version of the ventilation system included a motor speed controller which was equipped with a RS485 serial interface (‘Altivar 28’ manufactured by Telemacanique®). This unit enabled the flow rate of air through the oven to be varied remotely from zero to approximately 0.9 m³ min⁻¹ thus allowing the temperature controller’s heating duty cycle to be optimised at 40 and 60% under all conditions.

The entire oven unit was housed within a modified shipping container, which also housed some of the logging electronics. Located at one end of the shipping container was a large diameter ventilation fan which during normal experiments, purged the container with clean air at a rate of approximately 8 m³ s⁻¹.

5.3.3.2. Power supply

Primary power was provided by a 15kW mains supply feed. Power was initially supplied to a caravan, housing the data acquisition, mains control and communications hardware within a temperature regulated environment. Power and digital communication cables extended from the caravan to the oven enclosure, a distance of approximately 35m. The separation of the critical electrical equipment from the main enclosure was undertaken to reduce corrosive impact of the chlorine gas.

Due to the unreliability of the mains supply, a 7.5kW standby generator (Leroy Sommer type LSA 3519) was installed to maintain electrical supply. The supply from the generator was electrically and mechanically interlocked from the mains grid as outlined under Australian Standard® (AS) AS 3000-1991, AS3010.1. Custom automation software was originally written using Microsoft Visual Basic (version 3.1) to control all instrumentation and machinery. All automated operations including the monitoring of the mains supply, the operation of the generator, the changeover from the mains supply to the generator supply and back to the mains were computer controlled. The fully automated laboratory was unattended during normal operation. Just prior to the 200kg measurements, the control software was upgraded and reprogrammed with Labview® (National Instruments scientific automation
language, version 5.1). Advantech® control hardware (PCL 818HG, PCL 730, PCLD 782B, PCLD 785B and PCLD 8115) was used for all automation.

The mains supply voltage and current were continuously monitored by the control computer software. The computer disconnected all equipment from the mains when the supply voltage fell below 220volts. It was found that during some power outage episodes, the mains supply could switch rapidly on and off at short intervals presenting an increased potential for equipment failure. Hence, to eliminate this problem, the control code included a minimum 'off' period of 20 seconds. Following a continuous mains interruption of 2 minutes, the generator would be started and brought 'on line' to power essential systems. The generator was then operated for a minimum period of 20 minutes, after which time, the power would be reconnected to mains supply if this remained uninterrupted for a continuous period of 5 minutes.

Power supply to critical equipment was filtered, stabilized ('Line-R® 1250' manufactured by American Power Conversion (APC®)) and maintained through two uninterrupted power supplies (UPS) (APC® 'Back-up Pro 420' and a SOLA® '520') connected in series. Experience gained from the bagasse field work (chapter 4) showed that a twin UPS configuration gave increased reliability over a single UPS unit. This was especially the case as the battery cells aged.

5.3.3.3. Temperature control.

During the first series of 40kg CAT measurements, the 'CAL Controls #3200' temperature controller was again used. This unit, however, could not be remotely programmed and was replaced with a 'Brainchild BTC 9200 PID temperature controller' (precision ± 0.1°C) just prior to the 200kg measurements. The Brainchild unit possessed an integrated RS-485 communication interface that allowed the logging computer to remotely control the unit. While the Cal Controls unit displayed excellent stability, the Brainchild unit displayed a diurnal shift in the set point temperature of up to 0.8°C. The problem was traced to less accurate cold junction compensation circuitry and hence, to eliminate this fluctuation, this controller unit itself was located within a temperature controlled
housing. The temperature within the housing itself was maintained using the ‘CAL Controls #3200’
temperature controller, but with a ‘PT100’ platinum resistance device (PTD). Through this
modification, the diurnal temperature variation was eliminated. Chromel-alumel thermocouples were
used as temperature sensors for the controller with up to 13 strategically placed junctions being used.
These thermocouples were connected in parallel to reflect a mean air temperature. While the use of a
PTD sensor for temperature measurement would have eliminated the diurnal thermal drift of the
temperature controller, the addition cost of this sensor combined with its destruction during a thermal
ignition event leading to the occurrence of flames made the thermocouple sensor a more economic
choice. The solid state relay driver output of the temperature controller, activated a master solid state
relay (SSR) powering four banks of heater elements. Each of the four parallel circuits was individually
switched with an independent SSR, allowing each circuit to be separately switched into the master
control circuit as required. By changing the number of heater units operating, the duty cycle of the
temperature controller could be optimised for improved precision.

5.3.3.4. Data logging

The output from each thermocouple wire was continuously and redundantly recorded throughout each
measurement. An industrial ‘field point’ module (Advantech® Adam 4018M, 16 bit resolution) was
used to electronically record the data to computer. Using statistical averaging, a precision of ± 0.1°C
was generally achieved from the logging device. Like the temperature controller, this module was
installed within a temperature controlled housing to reduce thermal noise from diurnal temperature
changes. Data was obtained in a serial form from the device through a RS485 serial interface, which
allowed the unit to be placed close to the point of measurement. Data also recorded upon a chart
recorder (TOA ‘Pegasus’ intelligent chart recorder, model INR 6082) which was housed within the
control caravan. Shielded thermocouple wire was used to connect the chart recorder to the oven
thermocouple sensors. Both recording devices possessed internal thermocouple cold junction
compensation and thermocouple linearisation algorithms. The custom logging software as mentioned
earlier, (section 5.3.3.2) was originally written by the author with Microsoft Visual Basic® (version
3.1), but this was eventually upgraded to Labview® (version 5.1).
Due to the unreliability of the telephone lines at the site, all communications were through the Global System for Mobile Communications (GSM) network with 'PC Anywhere' used to remotely access the instrumentation.

5.4. Procedures

5.4.1. Detailed description of the Critical Ambient Temperature measurements.

This section provides a detailed description of the experimental method used to determine Critical Ambient Temperatures (CAT). These procedures were used to undertake the CAT measurements that will be discussed in chapters six and seven. The method has been described in detail by Bowes (1984, page 186-189, 471). As stated in section 4.6.2, the method involves systematically exposing fresh samples of a reactive material to different ambient temperatures enabling the lowest temperature at which thermal ignition occurs and the highest temperature at which thermal ignition fails to occur to be determined. The geometry and the mass of the sample in maintained constant for each individual CAT series enabling the accurate correlation of the experimentally determined CAT with current thermal ignition theory. The measurements are completed within a thermally homogenous and temperature controlled oven with the accuracy of the reported CAT being a function of the thermal accuracy and precision of the temperature controller, the degree of homogeneity within the oven and the precision of the temperature difference between the lowest measured temperature where thermal ignition occurs and the highest temperature at which thermal ignition fails.

The CAT values in this thesis were determined through a process of 'bracketing'. In some cases, the oven temperature of the first trial measurement for a particular geometry and mass was determined through an 'educated guess', at other times, thermal ignition theory (Frank-Kamenetskii, 1969) was used to determine the optimal initial trial temperature. Further trial measurements were undertaken at different temperatures until the critical ignition temperature was identified to an arbitrary precision. The CAT is reported as the arithmetic mean between the lowest temperature at which thermal ignition occurred and the highest temperature at which thermal ignition failed to occur, while the experimental
uncertainty is reported as half of the difference between the two bracketing temperatures. The uncertainty of the reported CAT provided gives an indication as to the number of trial experiments completed, for example a reported uncertainty of ± 0.5°C would typically require in excess of seven individual trial measurements. The latter components of this section provide detailed descriptions of the individual procedures used to complete the CAT measurements.

5.4.2. Instrumentation of the sample drums.

Samples were instrumented with at least one chromel-alumel thermocouple junction (fibreglass braid over 0.5 mm fibreglass insulated conductors or fully polytetrafluoroethylene (PTFE) coated) placed at the geometric centre of the drum. All thermocouple junctions were flame formed using an ‘oxy-acetylene torch’. In the case of PTFE sheathed thermocouple wires, the bared wire was hot dipped into molten PTFE, thereby, maintaining the integrity of the insulation. When required, samples were instrumented with extra thermocouples that were placed to give information regarding the radial temperature gradient within the sample drum. Each drum was instrumented by firstly cutting the manufacturers seal and then transferring approximately half of the contents into a clean drum. This secondary drum was of an identical type to the original HDPE drum and was rinsed only with distilled water and air-dried. Extreme care was taken to eliminate sample contamination during instrumentation. One or more clean chromel-alumel thermocouple wires were initially drawn through a small hole pierced through the sample drum at a position 25mm below the top rim of the drum. The thermocouple junctions were placed vertically at a level approximately half the depth of the drum. If one thermocouple junction was used, then it was placed at the centre of the drum. If more then one was used, then the second thermocouple junction was placed at a radius of approximately 5.5cm and a third placed so that it was in contact with the inside wall of the HDPE drum. The drum was next carefully refilled with calcium hypochlorite from the secondary drum, the lid secured and the instrumented drum then carefully placed into the preheated oven. Figure 5.4.1 shows the installation of thermocouple junctions into a 40kg HDPE drum.
The 36kg measurements were prepared in a similar manner to the commercial drums except that an orthodox stainless steel mesh equicylinder (0.175m radius) was used and thermocouple positions were changed. In this case, three radial thermocouples were embedded at a radius of half the height of the basket at radial distances of 6 cm and 11.9 cm, while a fourth thermocouple was placed on the inside face of the gauze. On one occasion the loading procedure was modified to reduce the time required for the sample to reach ambient oven temperature. In this case, the hydrated HCH was loaded into a number of clean stainless steel cylinders with a diameter of 8cm and a length of one metre, and heated to within two degrees of the oven air temperature, in a separate oven. The hydrated HCH was then loaded into the gauze basket and instrumented in the above manner at the elevated temperature. While this method reduced the warm up time to less than 12 hours, the quantity of chlorine evolved during the loading and instrumentation operation, made this method a dangerous undertaking and it was not continued. This method also had the disadvantage of not giving any useful data about the warm up time and heating behaviour. Hence, the data recording commenced after loading into the gauze basket, when the initially hydrated HCH was two degrees Celsius below the oven temperature. Figure 5.4.2 shows a view of the 35kg gauze basket through the transparent acrylic panel.
5.4.3. Loading

The instrumented drum was placed on a timber sheet, which was itself supported by hollow blocks 150mm thick. This support allowed a free flow of air under the timber board. For still air experiments, a steel box (2mm wall thickness) was placed over the drum and located in a position so that it did not touch the HDPE drum. The steel box had been accurately fabricated and fully Metal Inert Gas (MIG) welded, so that the bottom edges formed a good seal with the flat timber board. After closing the oven door and energising the heaters and circulating fan, the drum was left undisturbed.

The procedure for loading and instrumenting the 200kg experiments was identical to the 40 kg experiments except that $5 \times 40$kg drums were carefully emptied into a clean 200kg fibre drum and
placed in position within the oven. For measurements involving more than one drum, the individual drums were loaded and instrumented in a manner identical to that discussed above. The drums were stacked in the appropriate configuration within the oven and when required, enclosed with the appropriate sized steel box.

5.4.4. Description of the Standard American Decomposition Test.

An overview of the SADT was given in section 4.6.1. Prior to commencing SADT determinations the oven described in section 5.3.3 was modified to be fully compliant with United Nations Series H test prescriptions. (UN, 1975: 28.4.1)

The sample drum was filled and instrumented using the procedure described above with a thermocouple placed at the centre of the sample. During SADT measurements, however, a stainless steel ‘thermowell’ (6.25 mm diameter) was used to contain and position the thermocouple at the centre of the drum. (UN, 1975: 28.4.1.2.6) Additionally, during SADT tests the temperature of the air surrounding the commercial drum of HCH was precisely measured using four precision Platinum Temperature Devices (Sensing Devices Limited – Band 5 precision PTD, tolerance 0.01°C) and monitored using the logging apparatus described in section 5.3.3.4.

5.5. Calibration

5.5.1. Temperature reference

The temperatures of the data logging equipment were calibrated against a Comark® KM45 handheld digital thermometer. This meter had been calibrated and referenced to TYPE K KM-PRO6 sensor (NATA calibration number 5961N, traceable to Australian National Measurement Standards via Primary Standard Platinum Resistance Thermometer (SPRT) serial number 213832 report number 40562). To eliminate the small thermoelectric differences between individual thermocouples (±1.5°C), all thermocouples were individually calibrated at the temperature of the particular CAT measurement.
Prior to and at intervals during criticality measurements, the above thermocouple meter and sensor probe were checked for drift by comparing the meter reading to the ice point and steam point of water at 1 atm. At no time during the experiments did the meter reading differ by more than ± 0.1°C.

5.5.2. **Spatial thermal distribution within ovens.**

During the initial commissioning of each oven and during all CAT measurements the spatial temperature distribution within each oven was measured. Initially within the large oven, the maximum temperature difference measured between the centre of the oven to any position 3cm from the walls, floor or roof was 2°C. Following the modifications for SADT compliance, the maximum temperature difference measured within the larger oven was reduced to 1.1°C. In both cases, the maximum temperature difference was measured in the vertical plane and no appreciable gradient found over a horizontal plane. It should be noted that the measured temperature differences between the centre of the oven and any radial position at a distance of 0.5m from the centre were much less than the above values, with these being typically less than 0.5°C. During the measurements discussed in section 5.3.3, the temperature distribution around the drum was measured manually. Thermocouple sensors placed in the stirred air stream above, below and at the sides of the oven at a distance of approximately 2cm from the drum or steel box, in the case of the measurements completed using natural convection. The measured temperature differences observed during measurements were less than 0.5°C.

5.6. **Heat transfer coefficient measurements**

5.6.1. **Heat losses from a 6m shipping container.**

A 'steady state' method was used to measure the heat transfer coefficient of a standard 6m shipping container. The method involves accurately measuring the electric power required to maintain the internal temperature of the shipping container at a constant, measured temperature above that of the exterior ambient air temperature.
A model ACC-1001-UP shipping container, serial number AMS/89 7799, identification number FBZU 624311 3 was used for these measurements. At the time of the measurements, the container was within the inspection period for cargo shipment. The container was levelled and supported 150mm above the ground at each of the four corners. Within the container, up to three banks of electrical heating elements were placed along the lengthwise centreline of the container at equally spaced intervals from the door end. Two of the heating banks consisted of 5 x 850 watt air heating elements while the third, consisted of a heater bank comprising of a 1100, a 1600 and a 2200 watt element. By connecting heater elements in differing combinations, the heating load could be varied from 850 watts up to 13kW. Three oscillating fans were placed between the heating banks to produce a gently stirred airflow within the container.

The temperature within the container was measured with four chromel-alumel thermocouples suspended within the shipping container away from the heater banks. These strategically located thermocouples were connected in parallel to reflect the mean temperature within the container.

While undertaking these measurements, care was taken to select stable and wind free weather conditions. In addition, the container was strategically positioned in an area of dense scrub that surrounded the container at a distance of 4m on three sides. The top level of the vegetation was higher than the top of the container and provided further wind resistance. Measurements were completed late at night when ambient temperature and the mains voltage supply were most stable. After sealing the container, the fans and heaters were energised and the temperature monitored, using a chart recorder, until thermal equilibrium was achieved. The time required to reach thermal stability was in the order of 2 hours for the lower heater power values and 4 hours for the higher power values. Once steady state was achieved, the outside ambient and the internal average container temperature were monitored for a further 15 minutes. The air temperature rise, due to the electrical heating, was calculated from the difference between inner average and outer average air temperature over the final 15 minute period.

The total power consumption of the heater/fan units was determined by simultaneously measuring the rms AC supply voltage and current flow. Two calibrated clamp current meters (Yokogowa model 2343-02 (resolution 0.01A); APPA model 33R (resolution 0.1A)) and two calibrated voltage meters
(Hoki model 3256 digital Multitester (resolution 0.1V) and a Jaytech QM1340 digital multimeter
(resolution 0.01V)), were used during the measurements. The power value was calculated from the
mean voltage and current values over the final 15 minute temperature measuring period. The results
were interpreted using Newton's Law of Cooling in the form:

\[ \chi = \frac{q}{A(T_c - T_a)} \]  \hspace{1cm} [5.1]

Where \( \chi \) is the convective heat transfer coefficient \( J s^{-1} m^{-2} K^{-1} \), \( q \) is the power and is equal to the
electrical input to the container while it is at steady state conditions. \( T_c - T_a \) are the temperature
difference between the inner container air temperature and the outer ambient air temperature, while \( A \)
is the surface area, including the floor, which was measured to be 76.1m².

5.6.2. Measurement of other heat transfer coefficients.

The heat transfer coefficient of a 40kg HDPE drum in still air, the 200kg fibre drum in still air, the
40kg drum within a close fitting steel box, the 200kg fibre drum within a close fitting box and the
40kg drum in fan forced air, were measured using the apparatus and methods described in this section.
Essentially the same type of steady state heat transfer method that was used in the section 5.6.1 was
applied to each of the above-mentioned drums. For each of the above measurements, the drum under
investigation was placed within a convection environment that was identical to that of the
corresponding CAT measurement. The vessel was filled with water to approximately the same level as
when loaded with hydrated HCH, and then fitted with a heating element, stirrer and thermocouple
sensor. The power consumption and temperature increase at equilibrium of each drum was measured
with the same instruments and in a similar manner to, the measurements of section 5.6.1. The 40kg
drums typically required 6 to 8 hours to reach thermal stability at each power value, while the 200kg
drums required in excess of 3 days.

5.7. Percentage moisture determination.

The moisture content of the hydrated HCH sample was determined gravimetrically by vacuum drying
the sample in the presence of phosphorus pentoxide until a constant mass was achieved.
Approximately 10 grams of sample was accurately weighed (±0.0001g) into a clean dry and pre-
weighed weighing jar. The samples were placed into glass desiccator jars containing either phosphorus pentoxide only, silica gel only or phosphorus pentoxide under vacuum. The moisture loss was monitored until constant mass was achieved.
Chapter 6

Results of Critical Ambient Temperature measurements upon single containers of hydrated High strength Calcium Hypochlorite

6.1. Introduction

This chapter describes CAT measurements upon HCH using different convection conditions and for a range of different container types. The first series of CAT measurements discussed were completed using an orthodox stainless steel gauze sample basket of equicylinder geometry, that is, geometry where the height and diameter of the cylinder are equal. The aim of these initial measurements was to normalise the larger sized CAT measurements of the current study to the laboratory size CAT experiments completed by Gray and reported in (Gray and Halliburton, 2000). The subsequent CAT measurements that followed the initial experimental series were completed using sample quantities and container types that are commercially used to transport HCH. During the ‘commercial size’ experiments, the influence of the convectional conditions, surrounding the commercial container was also investigated.

The uncertainties reported for the experimental ambient temperature of all the data sets in this chapter section are standard deviations of the recorded data or the uncertainty of the instrumentation/calibration method, whichever was the greater value. Hence, uncertainty values give a reflection of the thermal stability of the apparatus used. Also, while each CAT reported in this chapter is generally a result of more than four individual measurements, for clarity, these data plots generally display only the most precise two measurements that bracket the reported CAT, that is, the minimum temperature at which critical behaviour is displayed and the maximum temperature at which sub-critical behaviour is displayed. All data plots except for figure 6.2.1 have been displayed with a reduced data set for presentation purposes with all data recorded to at least 1 minute time intervals.
6.2. Chemical Composition of hydrated HCH sample used in this current study

The hydrated HCH sample used in this current study was chemically analysed to determine whether its chemical composition was within the range specified by UN 2880. The results of the analysis are shown in table 6.1.

Table 6.1 Results from the chemical analysis of the hydrated HCH sample used in the current study

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Percentage composition by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OCl)₂</td>
<td>63.4</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>6.83</td>
</tr>
<tr>
<td>Ca(ClO₃)₂</td>
<td>4.29</td>
</tr>
<tr>
<td>NaCl</td>
<td>14.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>8.45</td>
</tr>
<tr>
<td>Other calcium salts</td>
<td>3.05</td>
</tr>
</tbody>
</table>

The chemical analyses, other than the moisture determination, were completed by T.M Flynn (Unisearch Research Centre for Chemical Analysis, University of New South Wales, Kensington, Australia) using American Standard Test Measure (ASTM) Designation: D 2022 – 89. The moisture determination was completed by the author of the current study using the three gravimetric desorption methods that are described in detail in section 5.7. The results of these measurements are shown in figure 6.2.1.
Figure 6.2.1: Percentage moisture of hydrated HCH as function of time during the drying measurements drying at 21°C.

Each of the three measurements shown in Figure 6.2.1 reached a constant mass corresponding to 8.45% water by mass (wet basis). The time taken for each sample to reach a constant mass, however, varied between the three drying methods. The drying period ranged from 5 days in the case of P₂O₅ under vacuum, to nearly 21 days in the case where silica gel was used as a desiccant. The chemical composition of the hydrated HCH used in the current study was determined to be within the UN2880 specification.

6.3. Critical Ambient Temperature measurements of 35kg of HCH

This section describes the initial series of CAT measurements that were completed using a conventional stainless steel gauze equicylinder basket of 0.175m radius and 35kg capacity. The apparatus described in section 5.3.1 was used, producing conditions of forced convection only. Each sample was instrumented with thermojunctions as described in section 5.4. For clarity, only the temperature at the centre basket position is shown in this figure. The results of these measurements are shown in Figure 6.3.1.
Figure 6.3.1: Sub-critical and super-critical time traces displaying the central temperature of hydrated calcium hypochlorite samples when contained within a conventional stainless steel gauze basket.

In an effort to reduce the total time required to complete the CAT measurements, the super-critical measurement whose results are shown figure 6.3.1 was completed using a variation to the orthodox CAT experimental procedure. Both of these procedures are described in detail in section 5.4. The modified method involved pre-heating the HCH sample in small containers to a few degrees less than that of the oven temperature required to perform the CAT measurement. Using this "classical" Frank-Kamenetskii (1969) method, the time required to complete the CAT measurement was reduced by approximately 28 hours. In executing this method, however, the author was exposed to very high local concentrations of chlorine gas at the time of test sample assembly. Due to safety concerns associated with exposure to high concentration chlorine gas, this procedure was only undertaken on a single occasion. The conventional CAT experimental procedure was subsequently followed for the sub-critical measurement.
The CAT measurement exhibiting sub-critical behaviour in figure 6.3.1 was completed using the standard procedure described in section 5.4 with an oven temperature of 60.6°C ± 0.2°C. The corresponding measurement displaying super-critical behaviour was completed at an oven temperature of 68.1°C ± 0.4°C. It should be noted that the installation of the thermoelectric junctions into the super-critical test sample was performed while the basket was being loaded with preheated HCH. After instrumentation, the basket was then placed into the oven using the standard procedure outlined in section 5.4. Manual temperature measurements were taken at arbitrary times only during the preheating phase, with electronic temperature logging commencing after the gauze basket was filled and instrumented. Hence, for comparison of the two sets of data 6.3.1, the time scale of the super-critical measurement has been offset by 28 hours, which is the same time period required for the sub-critical measurement to heat to the same temperature.

Due to an instrumental problem, the super-critical run was terminated shortly after a clear upward temperature inflection was displayed, but before the maximum temperature rise was achieved. The data displayed in figure 6.3.1, however, shows a clear divergence between the sub-critical and super-critical heating behaviour. In the sub-critical case, the centre temperature of the basket increased to a maximum of 25°C above the oven air temperature before falling as the HCH reactant was consumed, whereas in the super-critical case, the centre temperature excess was more than 70°C.

Figure 6.3.2a displays the temperature history of the super-critical basket at the centre position, mid radius position and edge position, while figure 6.3.2b shows temperature history of the sub-critical basket at similar spatial positions.
Figure 6.3.2a: (top) and 6.3.2b: (bottom): The super-critical (top) and the sub-critical (bottom) temperature time profile for the 35kg stainless steel gauze basket. Ambient air temperatures were 68.1°C ± 0.4°C for the super-critical case and 60.6°C ± 0.2°C for the sub-critical case.

Both 6.3.2a and 6.3.2b show the usual heating behaviour in each case, with the temperature at the centre basket position remaining at a spatial minimum during the warm-up period, then eventually reaching the spatial maximum temperature as the temperature excess and run time increases. For each measurement, the edge temperature thermocouple sensor was positioned approximately 2 millimeters below the gauze/hydrated HCH surface.
The evolution of the sub-critical heating profile is shown in figure 6.3.3.

Figure 6.3.3: The evolution of the temperature time profile for the sub-critical 35kg stainless gauze run. Ambient air temperature = 60.6 °C ± 0.2 °C

The composite family of curves in figure 6.3.3 shows the temperature profile of the sub-critical measurement at hourly intervals for the period four hours before the centre thermocouple reached ambient temperature and ten hours following. Notice the edge temperature of the basket remains essentially at the oven temperature (<1 °C increase above oven temperature). This small edge temperature rise as well as the overall general shape of this profile, are indicative of a material with a very high Biot number. (This aspect will be discussed later in this chapter) The profile of the super-critical experiment has not been shown since the basket profile shape was artificially modified by the non-standard filling process. By filling the basket with sample that had been pre-warmed to within
3°C of the oven air temperature, the profile across the basket was of nearly uniform temperature as it warmed above ambient temperature.

The behaviour shown in figure 6.3.3 was also displayed during the small scale, profile type, measurements completed by B.F Gray and reported in Gray and Halliburton (2000). This behaviour will be discussed in detail later in this chapter.

6.4. Critical Ambient Temperature (CAT) measurements of 40kg commercially transported high-density polyethylene containers using conditions of forced convection.

This section describes the first series of CAT measurements of hydrated HCH when contained within commercially available HDPE containers of 0.175m radius, 0.44m height and 40kg capacity. The sample was instrumented in the usual manner with thermojunctions and the HDPE container sealed. The HDPE containers were used in an ‘as arrived’ state and were filled by the manufacturer. It was noticed that at the top of each container was an air space of approximately 4cm between the uppermost level of the hydrated HCH and the lid of the closed container. The results of these measurements are shown in figure 6.4.1.
Figure 6.4.1: Two super-critical time traces displaying the central temperature of 40kg of hydrated calcium hypochlorite contained within a 0.175 m commercial HDPE container.

The CAT results shown in figure 6.4.1 were obtained using the apparatus described in section 5.3.1. The measurement at 60-1°C ± 0.3°C was undertaken using a standard laboratory oven without modification, while the measurement at 59.8°C ± 0.2°C was undertaken using the modified oven, again described in section 5.3.1. The data in the above figure display two ‘critical conditions’. The first critical condition is shown by the CAT trace at an oven temperature of 59.8°C, where the hydrated HCH self-heats to >150°C and then levels out. In this first case, the experiment was super-critical with respect to the hydrated HCH only, although visually, the HDPE container showed signs of melting and charring. The second critical condition is shown by the CAT trace at an oven temperature of 60.1°C. In this second case, the hydrated HCH self-heated to approximately 175°C and remained at that temperature for approximately 30 minutes before the HDPE ignited, whereby the sample temperature increased to approximately 1000°C. Following the ignition of the HDPE in the second case, the HDPE container, the laboratory oven and temperature controller were destroyed in the associated flames. Clearly, in this second case, the experiment was super-critical with respect to both the hydrated HCH and the HDPE.
The evolution of the heating profile for the 59.8 °C 40kg HDPE measurement is shown in figure 6.4.2.

![Diagram showing temperature profiles over time and radius](image)

**Figure 6.4.2: The evolution of the temperature time profile for the 40kg HDPE measurement at 59.8 °C.**

The composite family of curves in figure 6.4.2 shows the temperature at hourly intervals for the period 6 hours before the first internal thermocouple measured ambient temperature and 12 hours following. The edge thermocouple sensor was positioned on the inner surface between the hydrated HCH and the HDPE container. Notice the different general shape of this current profile to that of figure 6.3.3. Notice also, that for a similar centre temperature rise, these current data show a larger surface temperature rise to the data shown in figure 6.3.3. These results suggest that the HDPE container offers a greater thermal resistance to that of the gauze basket, an aspect that will be discussed late in this chapter.
Figure 6.4.3 displays the combined data from the 35kg gauze CAT measurements and the 40kg HDPE CAT measurements that were both completed using conditions of forced convection.

![Combined centre temperatures](image)

**Figure 6.4.3: Combined temperature time traces for 40kg HDPE measurements and the 35kg gauze measurements.**

The four sets of results that are shown above display both super-critical and sub-critical behaviour. The results show nearly identical rates of heating for the first 45-hour period, during which time it is not possible to predict the final experimental behaviour type until a period of 48 hours has passed in the super-critical gauze case, and nearly 60 hours in the sub-critical gauze case.
6.5. CAT measurements of 40kg commercially transported HDPE containers of hydrated HCH using conditions of natural convection.

The second series of CAT measurements were also completed using commercially available HDPE containers of hydrated HCH, but this time, using conditions of natural convection. The large-scale apparatus discussed in section 5.3.3 was used in conjunction with an identical type of hydrated HCH sample and an identical type of HDPE container to that used in section 6.4. The standard procedures described in section 5.4 were followed, however, this time a close fitting steel box (0.41 x 0.41 x 0.48m) was placed over the HDPE container. Figure 6.5.1 displays the temperature time traces of the centre thermocouple for five 40kg HDPE CAT measurements, which were completed using still air conditions.

![Graph showing temperature-time traces](image)

*Figure 6.5.1: Sub-critical and super-critical centre temperature time traces of CAT measurements for 40kg of hydrated calcium hypochlorite contained within a 0.175 commercial HDPE container using conditions of natural convection.*
The experiment at a temperature of 54.5°C was completed much later than the other four measurements and used a separate batch of fresh hydrated HCH. Also during this measurement at 54.5°C, the remote logging unit ‘hung’ from the 42nd hour to the 61st hour and since the chart recorder, which was generally used to supplement the electronic logging system, was required for a separate experiment, no temperature data was obtained for this period. However, all other equipment continued to operate during this time period. These data display the usual divergence between sub-critical and super-critical behaviour, however, the CAT measured using these still air conditions, is now 5°C lower than the CAT for the corresponding forced convection case. These data display similar heating paths for both the sub-critical and the super-critical case up until the time where the curves diverge, with no differentiating behaviour being evident until approximately 50 hours after commencing the run. Furthermore, predicting the self-heating behaviour becomes increasingly difficult as ambient temperature approaches criticality, with no distinguishing behaviour displayed between measurements at 53.9°C and 56.6°C for nearly 60 hours. A similar type of heating behaviour during the initial heating/induction period for both sub-critical and super-critical experiments was a common observation for all data in this study.

While the temperature time traces at 53.9°C and 56.6°C display definite sub-critical and super-critical behaviour respectively, the type of behaviour at 54.5°C is less definitive. The nature of the thermal behaviour at 54.5°C is less defined with subtle features suggesting that this run is either very close to or just above criticality. These features include: the definite upward inflection with temperature until the computer ‘hung’ at 44 hours (notice that this is upward inflection is similar in behaviour to the corresponding upward inflection of the 56.6°C data), an integrated trace area (with respect to oven ambient temperature up until the time of the maximum temperature rise), that is only 15% less than the 56.6°C run, as well as a subtle upward inflection at a time of approximately 90 hours that gives a suggestion of accelerative behaviour. Clearly, using the definition of Gray (1975), this run is in, or approaching, the sensitive experimental region of this system. This 54.5°C measurement was completed after publication of the other results in figure 6.3.1 (Gray, B.F. and Halliburton, B., 2000)
results of the 54-5°C measurement was also well within the uncertainty of the published results Gray and Halliburton (2000), the CAT in this current study will continue to be reported as 55-2°C ± 1-3°C.

Figure 6.5.2a displays the exterior surface history during a normal CAT measurement upon an unopened 40kg HDPE container of hydrated HCH. Figure 6.5.2b displays the centre temperature and the exterior surface temperature of a normally instrumented, but otherwise identical, 40kg HDPE container of hydrated HCH. Both of these containers were also heated using identical environmental conditions.

![Graph showing temperature over time](image)

Figure 6.5.2a: Unopened, externally instrumented 40kg container of hydrated HCH, as shipped, at an ambient temperature of 58.1°C.
Figure 6.5.2b: Centre, half radius and ambient temperature time traces of an identical HDPE container of HCH at an ambient temperature of 56.6°C ± 0.4°C.

Figure 6.5.2b displays the results of a internally instrumented 40kg container displaying super-critical behaviour. In this case, the centre temperature reached 190°C, while the outer surface temperature reached 130°C. Figure 6.5.2a displays the results of a similar 40kg container, but this time the measurement was performed with no internal thermocouples and hence, no possibility of either contamination or thermocouple catalysis. (This test was completed with the manufacturers seal unbroken.) Two thermocouple sensors were taped to the exterior of the container at positions 1/3 and 2/3 of the container’s height and as shown in the above figure, displayed the characteristic super-critical behaviour. Inspection of each container at the conclusion of each measurement revealed similar degrees of melting and charring suggesting that the inclusion of the chromel-alumel thermoelectric junctions did not significantly affect the self-heating of the HCH.

It should be highlighted that the temperature histories of the two exterior thermoelectric junctions displayed in Figure 6.5.2a exhibits behaviour that is not consistent with that of a purely conductive solid. In the purely conductive case, heat transfer would develop in a radial manner from the centre of
the container and as such, the two similarly placed thermoelectric junctions would be expected show identical temperatures. This is clearly not the case in figure 6.5.2b, as the temperature difference between the thermoelectric junctions located at the upper surface position and the lower surface position was measured to be 46°C (126°C cf. 80°C). These data clearly suggest the existence of convectional heat transfer within the HCH and given the granular nature of the HCH, this is not an unexpected observation.

6.6. Critical Ambient Temperature (CAT) measurements of 200kg quantities of HCH using conditions of natural convection.

The third series of CAT measurements involved 200kg quantities of HCH. These measurements were completed using commercially available, aluminum lined, fibre drums that are normally used for transporting hydrated HCH. The drums, of 0.275m radius, were filled with HCH and instrumented in the usual manner, as described in section 5.4.1. The measurements were completed using natural convection, though the use of a close fitting steel box, the dimensions of which for these measurements were 0.612m x 0.612m x 0.952m. The CAT measurements described here were essentially identical to the measurements described in section 6.5, except for the larger quantity of material and larger steel box.

The first measurement in this series was commenced at an initial temperature of 36.4°C. This starting temperature was determined by the usual Frank-Kamenetskii (1969) extrapolation of the combined results of Gray and the current gauze basket and HDPE results, up to the size and geometry of these larger drums. At the commencement of this first measurement, a detailed study of the heat transfer coefficient of the 200kg fibre container had not been completed and hence, this temperature was an approximate value only. The first run self-heated by only 2°C and required over 100hrs to reach the oven temperature from its initial temperature of 18°C. Since reactant consumption was expected to be low at these temperatures and self-heating rates, and to conserve sample supplies, the temperature was
raised to 44.7°C. This change was done without recharging the container with fresh sample, as is the usual procedure. Hence, it would be expected that these data would be conservative compared to the use of fresh HCH. Following the temperature increase, the sample self-heated to give spectacular results as can be seen in figure 6.6.1

![Temperature vs Time Graph](image)

**Figure 6.6.1:** Initial measurement of a commercial 200kg fibre drum in a steel box (natural convection). Measurement initially commenced at 36.4°C but was raised to 44.7°C after 300 hours.

Figure 6.6.2 shows three experimental runs spanning criticality. The trace displayed in figure 6.6.1 has for clarity, been displayed as two separate measurements, with the super-critical case offset in time to account for the warm up period from 18°C to 36.4°C.
Figure 6.6.2: Three temperature time traces spanning criticality for 200kg of hydrated HCH. Measurements were completed within a 0.275m radius fibre container using conditions of natural convection.

Figure 6.6.2 displays the usual sub-critical and super-critical divergence. Following the super-critical measurement, initial observation of the fibre drum revealed only localised discolouration of the material, however, closer observation revealed that the drum fibre had become very brittle, with the drum disintegrated into pieces when attempts were made to remove the drum from the oven. Some areas of the drum surface disintegrated when touched and offered no resistance to even light penetration of an object.

Figures 6.6.3 shows the super-critical profile across the drum.
Figure 6.6.3: Temperature time traces of the super-critical 200kg measurement showing the heating history of the drum at the centre, 14cm radius and the inside edge of the drum. Ambient temperature was 44.6°C ± 0.7°C.

The small fluctuation of the above oven temperature trace at the time of criticality, is a result of the delay between the temperature controller sensing the additional heat entering the oven airspace from the self-heating of the hypochlorite sample and responding by increasing flow rate of cool air in and through the oven. It can be seen that the temperature overshoot was quickly corrected, even with the large amount of extra heat entering the oven.

The evolution of the spatial temperature profile at 20 hourly intervals from a time of 50 hours until 230 hours, is shown in figure 6.6.4.
Figure 6.6.4: Evolution of the spatial temperature profile for the sub-critical 200kg measurement at distances from the centre of the drum. Ambient temperature was $42.2\, ^\circ\text{C} \pm 0.5\, ^\circ\text{C}$.

The family of curves in figure 6.6.4 displays spatial profiles that are similar to those of the 40kg HDPE, but differ from those of the 35kg gauze basket measurements. Whereas the 35kg gauze basket showed the first temperature increase at a position of 2/3 of the basket radius, the 40kg and 200kg CAT measurements displayed a maximum temperature excess at the centre of the drum at all times. Notice also that these current data display a larger edge temperature rise than both that of the gauze basket and the HDPE drum, but a with a lower corresponding centre temperature rise. (This heating behaviour will be discussed in detail later in this chapter)
6.7. Standard American Decomposition Temperature (SADT) measurements of 192kg commercially transported fibre drums.

This section describes SADT measurements involving commercially transported 192kg quantities of hydrated HCH. These measurements were completed using commercially available, aluminum lined, fibre drums that are normally used for transporting HCH. The drums were representative of the containers used for commercial use as required by the UN protocol. (UN, 1975: 28.4.1.2.1) The drums were identical to those used for the CAT measurements described in section 6.6 and were filled with hydrated HCH and instrumented in the usual manner, as described in section 5.4.1. Additionally, for these current measurements, a stainless steel thermowell was used to contain and position the thermocouple at the centre of the drum. (UN, 1975: 28.4.1.2.6) It should be noted that these measurements were completed in strict adherence to United Nations guidelines, Test H.1: United States SADT test. (UN, 1975: 28.4)

It should be noted that while 200kg quantities of HCH were used for the above CAT measurements, 192kg quantities are commercially transported. This mass difference originated as a result of the CAT measurements described in section 6.6 being completed at much earlier date that the current SADT measurements. The mass value of 200kg was arbitrarily selected for convenience early in this study and while this mass difference is of no consequence for the CAT measurements, since any known mass or geometry may be used, it is a problem for SADT measurements where the commercially transported quantity must be use. Hence, only qualitative comparisons will be made between the large scale SADT and CAT measurements. The results of this measurement is shown in figure 6.7.1.
Figure 6.7.1: Temperature time traces of SADT tests of 192kg commercial drums of HCH.

Figure 6.7.1 shows three SADT tests with the two measurements at 48.0°C being repeat measurements. These data show clearly that the 192kg drum has failed the SADT test at 48.0°C but passed at 47.0°C. Hence, the reported SADT is 48.0°C. Given that the measured CAT for a 200kg container of HCH in still air and within a steel box was measured to be 43.4°C, this result presents significant safety concern to the maritime industry.
6.8. **Summary of Critical Ambient Temperature measurements – 35kg to 200kg**

The CAT measurements of hydrated HCH for sample sizes of 0.175m and 0.275m radius are summarised in table 6.2.

**Table 6.2.- Summary of Critical Ambient Temperatures**

<table>
<thead>
<tr>
<th>Radius</th>
<th>Critical Ambient Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.175 (stainless gauze equicylinder, 35kg)</td>
<td>64.0 ± 3</td>
</tr>
<tr>
<td>0.175 (HDPE, height = 0.44m, 40kg)</td>
<td>60.1 ± 0.5</td>
</tr>
<tr>
<td>0.175 (HDPE, natural convection)</td>
<td>55.2 ± 1.3</td>
</tr>
<tr>
<td>0.275 (fibre, natural convection, height = 0.83m, 200kg)</td>
<td>43.4 ± 1.3</td>
</tr>
</tbody>
</table>

The CAT values in the above table have been calculated in the usual manner by calculating the arithmetic mean of the highest temperature at which thermal ignition occurs and the lowest temperature at which thermal ignition fails to occur.

6.9. **Heat Transfer Coefficient measurements.**

In order to correctly interpret the self-heating behaviour of hydrated HCH, both the conductivity of the hydrated HCH and the heat transfer coefficient of each sample container was measured. The heat transfer coefficient of each container or container/steel box assembly was measured using the steady state heating method described in section 5.6.2. Heat transfer coefficients of gauze baskets in laboratory ovens with forced airflow have been measured by Griffiths et al (1985) and Jones (1999), using spatial temperature profiles of bagasse and woodflour. Consequently, a $\chi$ of 14.0W/m$^2$K seems to be the most appropriate value for the basket CAT experiments in this current study. This aspect will be discussed further later in this chapter. The results of these measurements are shown in table 6.3.
Table 6.3 Heat transfer coefficient for gauze and commercial containers.

<table>
<thead>
<tr>
<th>Container type</th>
<th>$\chi$ (natural, W/m²K)</th>
<th>$\chi$ (forced, W/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36kg gauze</td>
<td>-</td>
<td>14.0$^a$</td>
</tr>
<tr>
<td>40kg HDPE</td>
<td>10.3 ± 0.4</td>
<td>16.4 ± 0.4</td>
</tr>
<tr>
<td>200kg fibre</td>
<td>7.9 ± 0.4</td>
<td>ND$^c$</td>
</tr>
<tr>
<td>Steel box$^b$</td>
<td>4.5± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ From Griffiths et al. and Jones.

$^b$ Steel box placed over the container to produce conditions of natural convection.

$^c$ Not determined as all 200kg CAT measurements were completed using natural convection.

The conductivity of hydrated HCH, in its usual granular form, was determined experimentally by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (Division of Building Construction and Engineering) using Australian Standard Test Measure (ASTM) C518 and ASTMC687. The values reported were 0.147 W/mK at 35°C and 0.142 W/mK at 23°C. It should be noted that both steel boxes displayed the same value for $\chi$.

6.10. Interpretation

The experimental results shown in table 6.2 have been interpreted in terms of the Frank-Kamenetskii model (1969). The standard tests for evaluating the suitability of this model for the interpretation of experimental thermal ignition data is the standard plot of $2\ln(T_{\text{ign}}/r)$ vs. $1/T_{\text{ign}}$. To aid in the interpretation of the data in this chapter, the work completed by Gray has been included in selected figures and has been identified as such. The standard Frank-Kamenetskii (1969) plot of the data in table 6.2 is shown in figure 6.8.1.
Figure 6.10.1: Frank-Kamenetskii (1969) plot of raw data. The measurements completed by the author of this current work are identified by the solid symbols and those by Gray and Halliburton (2000) identified by the hollow symbols.

These data shown in figure 6.10.1 display a good fit to Frank-Kamenetskii (1969) theory from about 120°C down to at least 40°C, suggesting that the decomposition chemistry below about 120°C is dominated by a single reaction regime.

The least squares fit to these data is approximated by the function:

\[
2\ln \left( \frac{T_{a,cr}}{r} \right) = (32.11 \pm 0.6) - \frac{(5.67 \pm 0.5)1000}{T_{a,cr}}
\]

which gives an apparent activation energy of 47 ±5 kJ/mol.

The higher temperature conductivity value has been used in all calculations in this current study as this value is more representative of the range of temperatures that is of interest to this current work. Using the standard formula \( Bi = \chi r/k \), the conductivity value at 35°C and the experimental heat transfer
coefficients shown in table 6.3, the Biot number for each commercial container size can be calculated. The results of this calculation are shown in table 6.4.

<table>
<thead>
<tr>
<th>Container type</th>
<th>Bi (natural)</th>
<th>Bi (forced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36kg gauze</td>
<td></td>
<td>16.6 ± 0.5</td>
</tr>
<tr>
<td>40kg HDPE</td>
<td>12.3 ± 0.5</td>
<td>19.6 ± 0.5</td>
</tr>
<tr>
<td>200kg fibre</td>
<td>14.8 ± 0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

The overall Biot number for each of the two assemblies, that is, where either the 40kg container or the 200kg drum was placed into a steel box and then, the complete ensemble placed into the oven, was calculated using the assumption that each of the two heat resistances operated in series. During measurements, the temperature differences between the steel box and the surface of the container were measured to be less than 0.5°C, a value sufficiently small for the above assumption to be valid.

Griffiths, et al (1985), have estimated the Biot number of gauze baskets by examining spatial temperature profiles during CAT experiments. This method involves measuring the temperature step between the basket/sample surface and ambient air, as well as the temperature differences within the sample normal to the surface. The above procedure can be applied to the data shown in figures 6.3.3, 6.4.2 and 6.6.4 using the relationship.

\[
\chi/\kappa = -(dT/dn)/(T_s-T_a)
\]  

[6.2]

where: \(-(dT/dn)\) is the temperature gradient within the sample normal to the basket/sample surface and \(T_s-T_a\) is the temperature step at the surface. This allows an estimate of \(\chi/\kappa\) and hence, the Biot
number, for each container type used in this current study. The results of this estimate are shown in table 6.5.

Table 6.5 - Evaluation of Biot number from Spatial Temperature Profiles for each container type.

<table>
<thead>
<tr>
<th>Container type</th>
<th>[-(dT/dn)/(T_e-T_a)/m-1]</th>
<th>Bi\text{profile})</th>
</tr>
</thead>
<tbody>
<tr>
<td>36kg gauze</td>
<td>340 ± 100*</td>
<td>&gt;50</td>
</tr>
<tr>
<td>40kg HDPE</td>
<td>101 ± 40</td>
<td>15 ± 6</td>
</tr>
<tr>
<td>200kg fibre</td>
<td>45 ± 20</td>
<td>7 ± 3</td>
</tr>
</tbody>
</table>

* The uncertainty in this value reflects the very small temperature rise measured at the basket surface.

The estimated Biot numbers shown in table 6.4 are generally less than the comparable Biot number value calculated using the directly measured values for the heat transfer coefficient and conductivity parameters. The lower value of Biot numbers in table 6.4 can be attributed to the limited number of thermocouple sensors used to determine the temperature gradient at the edge. The temperature gradient term was calculated using the difference between the exterior surface temperature sensor and the mid radius temperature sensor. Hence, it would be expected that this gradient, which is essentially a secant of the spatial temperature profile, would be less than the tangential gradient at the basket edge. The uncertainties reported for the above values reflect the limited amount of temperature data and the small surface temperature rises, however, this considered, the correlation between both of the above methods for the commercial containers is satisfactory. It should be noted that Griffitths et al. (1985) used significantly higher thermocouple density for the thermal gradient determination than the current work.

While agreement between the two methods of estimating Biot number shows some agreement for the commercial containers, this is not the case for the gauze basket. The thermal profile shown in figure
6.3.3 suggests that the Biot number for the gauze basket when filled with HCH, is higher than that measured by Griffiths who examined bagasse and woodflour. This result is not unexpected as HCH presents a different surface type to a moving airflow than either bagasse or woodflour. HCH presents a much more granular and porous surface to the oven airflow, a feature that may increase the effective surface area. Correspondingly, it would also be expected that bagasse and woodflour, when compressed, would present a surface that enabled less penetration of the oven airflow. Clearly, to be confident in the Biot number of the HCH filled gauze baskets used in this study, significantly more work is required.

The Frank-Kamenetskii number, at infinite Biot number, was calculated for both the 40kg and 200kg containers using the formula presented by Bowes (1984) that accounts for the geometry of the sample. For the 40kg HDPE container, $\delta_{cr}^m = 2.53$, while for the 200kg fibre drum, $\delta_{cr}^m = 2.37$. For calculations involving the 35kg gauze equicylinder, $\delta_{cr}^m = 2.764$ has been used (Bowes, 1984, table 3.2). The above Frank-Kamenetskii numbers were further corrected for finite Biot number using the formula obtained by Barzykin et al (1966) and Herhanov (1959) and presented in Bowes (1984). The corrected Frank-Kamenetskii number, as well as $\ln \delta_{cr} + 2 \ln (T_{ac} / r)$ [1.17] have been calculated from table 6.1 and are shown in table 6.6.

<table>
<thead>
<tr>
<th>Radius</th>
<th>$1000 / T_{acr}$</th>
<th>$\ln \delta_{cr}$</th>
<th>$\ln \delta_{cr} + 2 \ln (T_{ac} / r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.175 (gauze)</td>
<td>2.967</td>
<td>0.899</td>
<td>15.88</td>
</tr>
<tr>
<td>0.175 (HDPE, forced)</td>
<td>3.002</td>
<td>0.829</td>
<td>16.08</td>
</tr>
<tr>
<td>0.175 (HDPE, natural)</td>
<td>3.047</td>
<td>0.54</td>
<td>15.61</td>
</tr>
<tr>
<td>0.275 (fibre, natural)</td>
<td>3.160</td>
<td>0.60</td>
<td>14.69</td>
</tr>
</tbody>
</table>

$^a$ height = 0.44m

$^b$ height = 0.83m
The results in table 6.5 have been displayed according to the equation 1.17, and are presented in figure 6.8.2.

\[ T_{a,cr} \text{ (°C)} \]

\[ \ln \delta_{cr} + 2\ln(T_{a,cr}/r) \]

\[ 1000/T_{a,cr} \]

**Figure 6.10.2:** Frank-Kamenetskii (1969) plot of data corrected for finite Biot number. The measurements completed by the author of this current work are identified by the solid symbols and those by Gray (2000) identified by the hollow symbols.

The corresponding least squares plot of the combined data gives the equation:

\[
2 \ln \left( \frac{T_{a,cr}}{R} \right) + \ln \delta_{cr} = -\frac{(5.85 \pm 0.22)}{T_{a,cr}} + (33.33 \pm 0.64)
\]

[6.3]

The correction for finite Biot number has reduced the deviations compared to the raw data presented in figure 6.8.1, with the corresponding apparent activation energy for the low temperature reaction now \(48.5 \pm 1.8\)kJmol\(^{-1}\). Using the analysis discussed in section 1.2.2, the pre-exponential heat production rate \(Q \Lambda'\), can be calculated. Using the above E/R value, the conductivity value, and a bulk density of 1.0gcm\(^{-3}\), the calculated value of \(Q \Lambda'\) is \(7.48 \times 10^9\) Wm\(^{-3}\).
The power at any temperature can also be calculated using the above value of $Q\,A'$, the activation energy and the Arrhenius equation. For example, at 40°C, the calculated heat production rate is 60W/m³. When this calculated power data is compared to the corresponding measured calorimetry value of 50 to 80W/m³ (Bibby and Milestone, 1984) at the same temperature, then a good agreement is observed.

Using the dimensionless temperature rise, $\theta_0 = 1.778$ (defined in section 1.2.2), the maximum adiabatic temperature rise for the classic Frank-Kamenetskii (1969) case is $1.778RT_0^2/E$, which has a value of 33°C. The maximum temperature rise was 24°C for the 35kg gauze equicylinder and 23°C for the 40kg HDPE container. Given the lower Biot number of these containers used in this study and the sensitivity of this temperature rise near criticality, these predictions show a satisfactory agreement.

6.11. Discussion

This current study has confirmed that the decomposition chemistry of hydrated calcium hypochlorite can be described by two parallel exothermic reactions, with each reaction obeying the normal Frank-Kamenetskii (1969) theory over a limited range of temperatures. From temperatures close to 120°C and extending down to at least 40°C, the chemistry of this material is dominated by a low activation energy reaction. It is this reaction that is suspected to be responsible for the high degree of self-heating displayed by HCH at temperatures below 120°C. At temperatures exceeding 120°C, the chemistry is dominated by a separate reaction, which necessarily has higher activation energy. This type of behaviour is not new and has been considered initially by Abramov, Vaganov and Samoilenko (1975) and is presented in Bowes (1984).

As stated earlier, to be confident in the Biot number of the HCH filled gauze baskets used in this study, significantly more work is required. As such, the Biot number value of Griffiths et al. (1985) remains the most reliable. The uncertainty of this value, however, does not add significantly to the
uncertainty of the activation energy value. This insensitivity arises due to the range of container sizes over which CAT experiments have been completed and by the use of commercial containers, whose heat transfer coefficients have been accurately measured. This relative insensitivity is shown in figure 6.10.1 where the CAT values for gauze baskets have been plotted in the usual way using Biot number values of 14, 20 and 50 for the gauze baskets in figure 6.9.1.

![Graph](image)

*Figure 6.11.1: Frank-Kamenetskii (1969) plot of data corrected using a range of Biot numbers*

Figure 6.9.1 shows that while the correction for finite Biot number is important for the basket tests of this study, the impact upon the uncertainty of the calculated apparent activation energy is relatively small. If a Biot number of 20 is assumed, then a 3% increase in apparent activation energy is observed, while if a high Biot number of 50 is used, then a 6.7% increase is observed.

While the results discussed above raise some questions regarding the appropriateness of the Griffiths et al. (1985) heat transfer coefficient value for hydrated HCH, at present this is the most appropriate value.
The CAT values for 40kg and the 200kg and the SADT for 192kg of HCH that have been measured in this study, have very significant ramifications for the safe transport and storage of this material. Measurements of air temperatures within the cargo lockers of container carrying ships, where the cargo locker can contain in excess of 100 x 6m long freight containers, can reach maximum temperatures of 47°C on some deck areas. These hull temperatures, however, vary diurnally and cool down to temperatures of between 21°C and 27°C at night (Bowes, 1968; Gray and Holleyhead, 1999). Hence, the average ambient temperature that cargo stored within the hull would experience, would be a time average of these temperatures with the average value being shifted towards the larger temperature during voyages through tropical waters. Even without considering that 80 x 192kg drums of this material are usually packed into a 6m long freight container, given the fact that the CAT of a single 200kg drum of hydrated HCH was measured to be 43.4°C ± 1.3°C and that the SADT for 192kg of HCH was measured to be 48.0°C ± 0.3°C, one must critically question the safety of transporting hydrated HCH at these quantities. This issue will be discussed more fully in the following chapter, where the bulk self-heating behaviour that occurs where large numbers of individually self-heating containers is examined.

The activation energy and intercept values of the high temperature reaction are reported in Gray and Halliburton (2000). These values are 57.02 ± 5.01 for the intercept and 5.85 x 10^3 K for the E/R value. Using these results, the corresponding QZ value for the high temperature reaction is 5.64 x 10^19 Wm⁻³. While clearly the high temperature reaction is significantly more exothermic than the corresponding low temperature reaction, the high apparent activation energy of this reaction, means that little contribution is made to the total heat balance at temperatures below 120°C. At temperatures that are consistent with hull temperatures aboard vessels, the contribution of this reaction to the heat balance, becomes negligible. For example, the high temperature activation energy suggests that at 40°C, the contribution to the heat balance from the high temperature reaction is only 0.065mW or <0.1% of the total heat production rate.
It is the usual practice to extrapolate smaller scale CAT data to larger sized bodies to predict critical ignition temperature. This is a valid and well-proven method for predicting CIT (defined on page 118) as long as it is known that a single reaction regime exists over the entire temperature range of the extrapolation. In many cases, however, it is not known whether the chemistry consists of a single reaction or parallel reaction regimes. Where this information is unknown, it is imperative that large-scale measurements be undertaken to verify the assumptions made regarding the nature of the chemistry over the temperature range which is of interest.

The usual Frank-Kamenetskii (1969) plot, corrected for finite Biot number, is shown in Figure 6.9.2 for both the high temperature and low temperature reaction regimes of HCH.

![Graph showing Frank-Kamenetskii plot](image)

*Figure 6.9.2: Frank-Kamenetskii (1969) plot of high temperature and low temperature data corrected for finite Biot number. The measurements completed by the author of this current work are identified by the solid symbols.*

The dashed line shows the extrapolation of the high temperature data down to lower temperatures with the predicted CAT values of 93°C for the 40kg sample and 85°C for the 200kg sample. This extrapolation clearly highlights the danger of using a limited amount of data for the prediction of large
scale self-heating behaviour and further strengthens the case for the full (freight container) size thermal ignition measurements.

The sensitivity of the CAT of commercial transport shipping containers loaded with HCH to the nature of the storage or transport environment, has also been demonstrated. When experiments were completed within a steel box with a wooden floor, the combined effects of the additional thermal resistance of the box, combined with natural convection conditions within the box, lowered the CAT of the HDPE drum by approximately 5°C compared to a similar drum measured using forced convection conditions (other parameters being constant). This sensitivity to the nature of the storage conditions is fully consistent with the usual Frank-Kamenetskii (1969) and Heat Transfer theory. However, while these two heat transfer effects, (heat loss across the box wall and the convection conditions at the surface of the drum) are coupled, they are separate effects.

If the natural convection condition of the drum is firstly considered, then the relatively high thermal conductivity of HCH (0.147 W/mK at 35°C and 0.142 W/mK at 23°C for HCH and 0.05 W/mK for agricultural materials such as cotton or bagasse) results in a Biot number which is within the range that is sensitive to the prevailing surface heat loss conditions. Hence, the CAT of the drum will be influenced by the convensional heat transfer coefficient at the drum’s surface. It is interesting to note that for the materials where the calculated Biot number is high, the CAT measured for both natural and fan forced experimental conditions would be identical, since heat loss is independent of the surface heat loss condition.

When the effect of the steel box is considered, the two gas/solid heat transfers which occur on each side of the box provide increased thermal resistance. Hence in this case, as the Biot number calculated for the drum itself tends to infinity, the calculated overall (composite) Biot number for the assembly does not tend to the calculated Biot number of a single drum. This finding itself has serious implications for the type of testing procedure that is used to determine the maximum ‘safe’ transport temperature of this material. This is clearly shown when the CAT of 200kg of HCH (43.4 ± 1.3°C) and the SADT of 192kg of HCH (48.0 ± 0.3°C) are compared. While a small contribution towards the
lower CAT value can be attributed to the mass difference, the experiments comparing CAT’s of 50kg of HCH in fan forced conditions (60.1 ± 0.5°C) and still air conditions (55.2 ± 1.3°C) suggest that CAT values may be lowered by 5°C as a result of changes in convectional heat transfer conditions. Hence, for reliable results, not only must the sensitivity of the critical ignition temperature of the material to the convection conditions be addressed, but also any wrapping that modifies the heat transfer coefficient of material or container, such as a shrink wrapping of outer containment vessel, must be accounted for.

The United States self-accelerating decomposition test (SADT test) is the traditional test that is used by transport regulators to estimate the ‘safe’ transport temperature of reactive substances. The SADT test, on face value, is experimentally similar to a CAT test where the test is completed using the normal transport container for the substance, rather than the traditional gauze basket. Given the finding of this current chapter, however, three fundamental weaknesses are revealed, which under certain conditions, could result in a reported SADT that is above the critical ignition temperature of the body. These weaknesses arise firstly from the arbitrary placement of a 6°C temperature rise upon the centre temperature excess of the test sample and secondly, by the placement of an arbitrary time limit of 7 days upon the run duration. Bowes (1984, p8) has discussed a similar weakness with the Mackey test, which was traditionally used to assess the thermal ignition hazard of fatty oils used in the wool industry. In the Mackey test, an arbitrary time limit and temperature rise is also specified. This limitation allowed reactive or otherwise ‘unsafe’ oils, with long induction periods, to pass the test and thus, be classified as ‘safe’. In the case where reactive oil was treated with an antioxidant, the induction period was extended beyond the arbitrary time limit so that the thermal rise was not detected within the run period. In a critical evaluation of the SADT test, Gray, Holleyhead and Halliburton, (1999) have identified reactive substances where the SADT test would report a SADT significantly higher than the critical ignition temperature.

The third weakness arises through the manner with which the SADT test attempts to account for the type of packaging used for transport. The SADT test attempts to address the influence of the type of packaging by defining that ‘The test substance and packaging should be representative of that intended
for commercial use.' (UN, 1975: 28.4.1.2.6). While this packaging aspect is imperative for materials of low Biot number, the test fails to account for the prevailing convection conditions that have been shown to significantly contribute to the heat loss term. If a package with a high Biot number is firstly considered, then the total heat loss is virtually independent of the package type and the convection conditions, since the resistance to heat flow occurs almost entirely within the material itself. For materials with a high Biot number, the package type is obviously irrelevant. If a package with a low Biot number is now considered, then the heat loss and hence, the critical ignition temperature, will be sensitive to not only to the package type, but critically, to the airflow conditions around the package. It is essential therefore, that for bodies with a low Biot number, that the airflow conditions around the test package must be accounted for. In this aspect, the SADT test is flawed. The UN document (UN, 1975: 28.4.1.2.3) describes the air conditions such that 'thermostatically controlled air circulation is provided so as to maintain a uniform air temperature within ±2°C of the desired temperature'. The vagueness of the above definition allows any air velocity past the sample container to be used so long as a ±2°C or less temperature difference is maintained within the oven. It should also be noted that a significantly large convectional airflow was required to keep air temperature differences with the larger oven within the UN guidelines of ±2°C. Hence, for a sample with a very low Biot number, the reported SADT would be a reflection of the size of the circulation fan used during the test, rather that a definitive measure of the critical ignition temperature during transportation.

The vagueness of the SADT definition that states 'The test substance and packaging should be representative of that intended for commercial use.' (UN, 1975: 28.4.1.2.6) gives rise to a further issue when the drums of containers of self-heating material are transported in either an enclosed or wrapped state, for example a shrink wrapped pallet of drums. While the drums may be transported in a wrapped condition, they would be commercially used as individual drums. Hence, it may be interpreted that the SADT tests should be completed on the individual drum rather than the transported assembly of drums. Clearly with the above definition, there is scope for reporting the SADT for conditions that are other than those that normally exist during transport. Additionally, it should be noted that the United States Federal Regulations (United States Department of Transport, 1998: section. 173.21) prescribe that materials with a SADT below 50°C are required to be transported within temperature controlled
shipping containers. Given that the SADT for 192 kg of HCH was measured to be 48.0 ±0.3°C, these quantities of HCH should, given the above regulation, be transported within temperature controlled shipping containers. As such, the transport of 192kg drums of HCH has contravened the above regulations.

Clearly it has been shown that by placing arbitrary limits upon the maximum temperature rise and the duration of the test, there is the potential for SADT to be unreliable. As such, there exists the potential for thermal ignition leading to fire if the reported SADT is unquestionably accepted as the 'safe' transport temperature for the substance under all transport conditions.

6.12. Conclusions

1. The current study has confirmed that the thermal decomposition of hydrated HCH involves at least two distinct reactions. Each reaction is individually consistent with Frank-Kamenetskii (1969) theory of thermal ignition over a limited temperature range.

2. The activation energy of the reaction that is dominant below 120°C is 48.5±1.8kJmol⁻¹

3. Biot numbers for commercial containers of hydrated HCH are in the region where the critical ignition temperature is sensitive to the surrounding heat transfer characteristics.

4. Correction for finite Biot number has improved the agreement of the raw experimental data to Frank-Kamenetskii (1969) theory.

5. The CAT of a 40kg container, measured using forced convection conditions in a temperature controlled oven, is 60.1°C while the CAT of an identical container, measured using conditions of natural convection, is 55.2°C.

6. The CAT of a 200kg drum, measured using conditions of natural convection, is 43.4°C.

7. The use of small-scale, and therefore high temperature data alone for the prediction of the critical ignition temperature for commercial quantities of hydrated HCH, will give incorrect values that may be up to 40°C above the critical ignition temperature.
8. The SADT test has the potential to report an unreliable and more importantly, report a less conservative; 'safe' transport temperature for a material with a low Biot number.

9. The results of the measurements described in this chapter, combined with the low activation energy, suggest that the critical ignition temperature of commercially shipped quantities (13 – 18 tonnes) of hydrated HCH may be in the temperature range prevailing within the holds of ships, particularly in tropical waters.

10. At the time of thermal runaway, HCH can produce sufficient temperature rise to ignite the HDPE containers that are commercially used to transport this material.