CALCIUM HYPOCHLORITE
A fire and explosion hazard
by
V. J. Clancey
Burgoyne Consultants Ltd.

SUMMARY

Commercial calcium hypchlorite has been the cause of fire and explosions in ships, in storage and elsewhere. A study was carried out on its properties to determine the causes of events which were clearly spontaneous. The variable, unstable and sensitive characteristics were demonstrated leading to a fuller understanding of its observed behaviour.

Key words: Calcium hypochlorite; hazards; fire; explosion; spontaneous decomposition.

INTRODUCTION

Calcium hypchlorite, $Ca(OCl)_2$, is a powerful oxidising agent used very widely for sanitising water. The commercial product, made by chlorinating a lime slurry is not a pure substance. It contains varying amounts of other salts depending on the particular raw materials and method of manufacture.

Its purity is described in terms of its oxidizing capacity, as, for example, "70% available chlorine". This is a misleading misnomer. The oxidising capacity, due to its oxygen, is expressed notionally as if it were chlorine. As a result the actual chlorine is half the nominal "available chlorine" and the actual amount of $Ca(OCl)_2$ is about equal to the nominal available chlorine. Thus in the above there would be about 70% actual $Ca(OCl)_2$ and 30% other salts containing 35% actual chlorine.

It is made, mainly in USA and Japan, and shipped in large quantities to countries with requirements for sanitising water supplies and swimming pools.

A few years ago there was a spate of serious accidents, six in two years, in ships carrying several hundred tons in steel drums, usually with plastic liners. Typically these seemed to occur in ships in tropical waters. For example in a ship crossing the Indian Ocean there would be a sudden explosion followed by fire which, because of the ready supply of oxygen, was of great damaging intensity. Other incidents had occurred in stores involving unopened drums which suddenly exploded.

We were called in to investigate.

CONTAMINATION THEORY

It is well known that calcium hypochlorite is very reactive. For example if a single drop of an easily oxidised oil or liquid such as glycerine is allowed to fall into a drum of the hypochlorite it starts an exothermic decomposition causing the whole contents to heat up and bubble like porridge boiling.

The largest maker in USA had in their records very many claims from customers of drums exploding or catching fire. The firm put these down to contamination for example using a scoop slightly contaminated with something like sun-tan oil. However, a careful study of their records showed some cases in which unopened drums seemed to have caught fire spontaneously. Contrariwise the firm for many years had stored their product in their warehouses without any spontaneous occurrences.

Some of the ship incidents seemed to preclude any possibility of contamination. For example one ship which was brand new and had never previously carried cargo loaded sound drums direct from the factory into a clean hold and there was said to be no spillage. On its voyage through the South China Sea there was an explosion which blew off and bent the deck beams.

In another case new full drums were stowed on deck while the ship was in harbour in Australia having come from USA. During the night the watchman saw one of the drums suddenly burst into flames.

BLEACHING POWDER INSTABILITY

Gill (1) reported many instances of apparently spontaneous heating and explosion of drums of bleaching powder (chloride of lime). "During the war years, 1917-19, on several occasions 800 pound drums exploded within 24 hours of packing; in some cases, within 5 or 10 minutes after the bleach was packed the drum would become so hot that the paint would be burned off it.....When shipped in car lots sometimes eight or more out of fifty-five drums would burst en route".

He ascribed to the bleaching powder the formula $CaCl_2O$ or $CaCl_2O_2$ and explained the instability as due to traces of oxides of iron or manganese, derived from the limestone, and possibly to the presence of calcium chlorate. The available chlorine was 30-35%.

HIGH-TEST CALCIUM HYPOCHLORITE

Robson (2) more correctly states that true bleaching powder is a complex and variable mixture of $Ca(OCl)_2$, $CaCl_2$, $Ca(OH)_2$ and water of crystallisation. The so-called "high-test" calcium hypochlorite with which we are concerned is virtually $Ca(OCl)_2$ with various double salts and sodium compounds, from the sodium chloride used in manufacture as the source of chlorine. In addition there may be small amounts of calcium chlorate formed by slow decomposition on exposure to moist air at room temperature.

The commercial product is clearly a complex and variable mixture. It is reasonably stable at ordinary temperatures losing perhaps 2% available chlorine per year. This decomposition is accelerated in the presence of carbon dioxide and about one-third of the loss is due to the formation of chlorate and liberation of chlorine. At the same time chlorine monoxide may be formed.

EARLY STUDIES

Kast and Metz (3) carried out an extensive study including heating to various temperatures with and without additives, and other tests to establish whether it was a hazard during transport.

Their general conclusion was that it behaves as an oxygen source like the nitrates but far behind the reactivities of ammonium nitrate and potassium chlorate. At ordinary temperatures it is judged to be adequately stable for storage and transport.

It will be noticed that no mention is made of any possibility of spontaneous decomposition. In fact they contrast it with the instability of bleaching powder.

Recent experiences contradicted their conclusion regarding its safety.

REPORTS OF ACCIDENTS

Various authors, e.g. Mandell (4), Cane (5), Clancey (6) and others have reported incidents some at least of which have the appearance of being spontaneous. Further similar reports have been received from South Africa, Australia, New Zealand, USA and elsewhere.

While it was clear that many incidents had been due to contamination the number which had occurred with unopened drums strongly pointed to another cause and did not justify the optimism of Kast and Metz.

EXPERIMENTAL

For the experimental studies five samples were obtained from different makers in three countries. These will be referred to as samples A, B, C, D and E. In each case several drums were obtained and tests were carried out separately on spot samples from the drums. Some of the drums had been in store for an indefinite length of time (referred to as "old" samples). In the cases of B, C and D further newly made samples were obtained (referred to as "new" samples).

The "available chlorine", nominally 70% was determined by liberating iodine from KI and titrating. The results are given in Table 1.

The physical characteristics were determined in terms of bulk density and sieve analysis. The bulk density results are summarised in Table 2.

The sieve analyses showed that, with the exception of sample D, the material was relatively coarse with little less than 250μ m and 70-80% greater than 500μ m, although there was some variation from drum to drum. Sample D was found to be more than 98% less than 250μ m.

X-ray diffraction studies were carried out to try to determine what species other than $Ca(OCl)_2$ and NaCl were present. In the absence of type samples for comparison it was not possible to identify those found, of which there were four. There were clearly differences. In particular two species were found in sample C which were not present in the others. A third species was also present in sample C, but only to a small amount in samples B and E and not present in samples A and D.

Chemical analyses were done to determine the amounts of metals other than calcium. The results are shown in Table 3. In addition a trace (less than 0·001%) of lithium was found in all the samples together with very slight traces of silicon, strontium and manganese.

There was some evidence that chlorates may enhance instability. Therefore determinations were made, the results being given in Table 4.

The heats of solution in water were determined. They were found to lie between 31 and 40 cals/g but there did not seem to be any significant pattern.

Sensitivity to impact and to impacted friction were determined. With the exception of sample A all the samples showed a very slight degree of sensitivity. Sample A was definitely less sensitive than the others. The sensitivity was thought not to be significant in practical terms.

A simple quick test for thermal stability was required. For this purpose one gram of sample in a test tube was held in a bath at 169°C and the evolution of gas recorded. The bath temperature was a few degrees below the nominal decomposition temperature. Typical results are plotted in Fig.I. Other tests showed that the time to runaway decomposition, as occurred with samples B and C, depended as might be expected on the quantity used in the test.

A small scale test was required to assess the possibility of spontaneous ignition in a drum during transport. A test similar to the U.N. Heat Accumulation Storage Test (7) was used. 400 g of sample in a special Dewar vessel was held at constant temperature for not less than 150 hours. Repeated tests were done to determine the lowest temperature at which the sample decomposed violently with an uncontrolled rise in temperature. Similar tests were done on some samples with water added. The results are given in Table 5.

The manufacturers of sample A informed me that their product decomposed spontaneously during storage at ordinary temperatures to lose about 2% available chlorine per year. Manufacturers of sample B said their's lost about 3-5% per year.

The latter gave rates of loss at other temperatures, e.g. 2% in 24 hours at 55°C; 6% in 24 hours at 65°C; 4-6% in 2 hours at 100°C. It may be noted that taking these data in pairs to calculate the activation energy gives values from about 18 kcal/mole to 29 kcals/mole and the frequency factor varies from 10^6 to 10^{14}. It would appear that in this temperature range decomposition is not a simple process.

Similarly DTA, and TGA studies yielded results which were inconclusive and difficult to interpret. It was apparent that the decomposition was complex, and that behaviour on a large scale was very different from that in the small scale tests. Thus using these data gives activation energies of 31 and 33 kcal/mole and frequency factors between 10^{13} and 10^{15}.

Two full scale bonfire tests were carried out. A commercial drum of sample B (50 kg) was placed in a standard bonfire. In one case the drum had a plastic liner. In the other there was no liner.

In the absence of a liner after a short time the lid was blown off and the contents spewed out partially decomposing like bubbling porridge. In the one with a plastic liner there was suddenly a very violent explosion which scattered granules widely.

Practical experience in ships and warehouses had shown that if one drum exploded it communicated to any adjacent drums so that a whole stow was involved.

Similar bonfire tests were carried out by Faust(8) on a hydrated product containing 65% available chlorine. Decomposition was gentle and did not cause any disruption.

A full scale SADT test gave a temperature of 64°C as the minimum.

DISCUSSION

When considering the data it is necessary also to take into account prior chemical data together with practical experience of accidents during storage and transport.

It is generally stated in the literature that the decomposition reaction is

$$Ca(OCl)_2(s) \rightarrow CaCl_2(s) + O_2(g) \quad \Delta H= -20·8$$
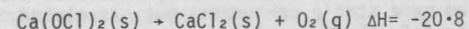
and that the decomposition temperature is in the range 160-180°C depending on rate and conditions of heating.

There is however clear evidence that the commercial product is unstable at ordinary temperatures slowly losing oxidising power during storage. There is also evidence that decomposition may follow other paths. For example chlorate is known to be produced during storage and actual loss of chlorine may occur.

The exothermic decomposition if started at one point (e.g. by adding a single drop of glycerine or inserting a smouldering cigarette) will propagate throughout the whole mass. The resultant temperature is high enough to ignite any combustible matter present which then burns vigorously in the oxygen evolved.

Practical experience over many years and involving large quantities has shown that normally the packaged material may be safely stored even under the highest ambient temperatures usually experienced. On the other hand there is firm evidence that complete unopened drums have spontaneously ignited. The frequency of these events is such that they must be considered to be rare and exceptional in some way.

The exceptional nature of the accidents poses a problem common to this class of investigation. The accident destroys the evidence in respect of the exception. Other samples obtained for laboratory studies are very unlikely to include exceptional, or rogue, product or conditions.

It was clear, from the results in Tables 1-4 and the X-ray crystallography, that there were differences between the samples. The old samples had lost varying amounts of "available chlorine" but in the absence of detailed histories it was not possible to deduce a degree of instability. The figures for the new samples did not differ much between them.

Bulk densities, and the related sieve analyses (not detailed here) showed differences but comparison later with the results of stability tests did not show any correlation.

In view of Gill's findings of the effects of oxides or iron and manganese, and possibly of chlorate, on the stability of bleaching powder, special attention was given to the presence of these and other metals (Table 3) and of chlorate (Table 4).

The first simple thermal stability tests gave results (Fig.I.) which appeared to be very significant. Samples B and C gave runaway decompositions after about 14 minutes which are almost identical and clearly different from the steady slow decomposition given by samples A and E. The former samples were higher in bulk density and slightly higher in iron, magnesium, aluminium and chlorate than the latter. These samples also showed on the X-ray studies the presence of three species not present in the more stable compounds, but, as already stated, it was not possible to identify these species.

The results of the Dewar vessel test (Table 5) gave perhaps the most interesting data which could be related to the potential behaviour of stacks of large drums.

Considering the results for new samples it will be seen that samples B and C gave runaway decompositions from 70°C. Sample D gave a value of 80°C. Old samples gave somewhat higher temperatures 110°C for A, 100°C for B, 80°C for C.

By applying the theory of heat transfer with knowledge of the parameters of the test vessel and of commercial drums it can be shown that a runaway decomposition may be expected with drums at an ambient temperature some 20° below those obtained in the Dewar vessels. Thus an ambient temperature of about 50°C could be expected to give the possibility of a runaway decomposition in a drum of material similar to samples B and C.

This calculation applies to a single drum. In the case of a close-packed stow of many drums in a ship's hold the dangerous ambient temperature would be considerably lower because of the restriction on heat loss.

Very little is known about the effects of close-packing of a large number of drums or of the diurnal variations of temperatures in a stowage.

If the close-packed drums could be treated as a solid cube thermal theory could be applied. For example Bowes (10) has pointed out that for calcium hypochlorite with a critical diameter of 1·1 m at an ambient temperature of 60°C the critical diameter is 4·3 m at an ambient temperature of 40°C. With air spaces between the cylindrical drums the dangerous ambient temperature would be higher by some indeterminate amount.

Bowes (11) also studied temperatures observed in ship's holds in the tropics. He pointed out that although peak temperatures as high as 70°C may be observed the relevant temperature to be considered was the mean maximum temperature during diurnal variations because of the thermal inertia of the mass. He found that the mean highest temperatures in the hottest parts of a ship's hold lay in the range 40°-50°C.

FULL SCALE DRUM TESTS

Some doubts must arise regarding the validity of the extrapolation from small scale Dewar vessel experiments to 50 kg drums. Uehara et al (12) carried out full scale tests with commercial drums and obtained a critical ambient temperature of 75°C for drums of 38 cm diameter, that is 50 kg. This compares very well with the values we obtained for sample B old which was made by the same manufacturer. Our figure of 100°C in the Dewar vessel reduces to about 80°C for a full size drum. But the same maker's new sample (B new) gave 70°C in the Dewar vessel which reduces to about 50°C for a full size drum.

What is not clear from this publication is the apparent variability of the commercial product. In previous papers these authors (13) had given very different values for the heat of reaction (from 20-30 kcal/mole), thermal conductivity (0·7 - 1·9 x 10⁻³ cal/cm sec.deg.) and other parameters used in the Frank/Kamenitski equation.

EFFECT OF WATER

The Dewar vessel tests with added water (Table 5) were carried out because it was believed that the hypochlorite was destabilised by water. Kirk-Othmer(14) states that the stability is

inversely proportional to the water content, the reaction yielding chlorine monoxide a dangerously explosive gas. Cane (15) believes that some, at least, of the recorded accidents may be due to the accumulation of chlorine monoxide which is then initiated by some small stimulus such as exposure to sunlight on opening a drum, or by mechanical shock. In this connection it is of interest that maker's instructions frequently advise to keep out of sunlight.

On the other hand a patent (16) was taken out for the addition of water to render the product more safe. Mandell (17) had described tests, using D.S.C. which give results supporting this claim. The amount of water added is in the range 7-10%. Calculations show that the endothermic effect of evaporating this amount of water is sufficient to prevent the temperature from rising above the self-propagating temperature.

The test results showed a lowering of the runaway temperature by adding water. Since a number of makers were proposing to market the "hydrated" form some further tests were necessary.

At my request bonfire and other tests were carried out in accordance with U.N. conditions; by Dahn of Safety Consulting Engineers (18). The results were satisfactory. An additional problem was whether by the temperature cycling which occurs during transport the water might migrate in a manner to leave part of the contents of a drum in the dangerous state of a small amount of water locally. Again at my request Faust and Milford (19) carried out prolonged temperature cycling followed by water determinations on spot samples at various points in the drum. They found there was no migration of water suggesting that the water was present as a hydrate.

Following these tests it was recommended to IMO that the transport of "hydrated" calcium hypochlorite be permitted under certain conditions. As a result an entry was made in the IMDG Code (20).

EFFECTS OF HANDLING

A number of accidents have occurred while, or immediately after, drums were moved, for example by fork lift trucks. These have occurred a long time after the product has left the factory. This might be explained by speculating that exposure to high temperatures in sunlight had started a self-heating process with a long induction period.

Another explanation seems possible. It is known that sometimes corrosion occurs in the drums due to failure of the plastic liner or of the lacquer coating of the steel which is sometimes used. Movement may then cause corrosion products to contact the hypochlorite and initiate a reaction, in the manner suggested by Gill (1) in the case of bleaching powder.

A third possible explanation is that chlorine monoxide had accumulated, as suggested by Cane (15) to an extent that it was sensitive to mechanical shock.

CONCLUSIONS

Commercial calcium hypochlorite is a variable product containing some 30% of other compounds. Its composition depends on variations in raw materials and details of the conditions of manufacture.

It is inherently unstable, capable of reacting exothermically. Its instability may be influenced by differences in its nature and of secondary compounds. Candidates as possible influences on stability are, inter alia iron, magnesium and organic matter from the limestone bromine from sea salt if this is used as a source of sodium hydroxide and chlorine, and water in small quantities. Another possibility is impurities introduced during manufacture or packing, or corrosion products within the package.

Observed incidents of apparently spontaneous explosion and fire are rare events and may therefore be ascribed to unusual, or rogue, drums - that is drums of which the contents are, for whatever reason, of lower stability or greater sensitivity than normal.

Since these are of rare occurrence it is most unlikely that samples available for testing will include such an abnormal material.

Test results indicate that many, possibly most, of the accidents involving unopened drums have been due to a low degree of thermal stability leading to self-heating after exposure to high ambient temperatures; such self-heating having possibly a long induction period.

Some incidents, possibly a few, have been due to the accumulation of sensitive decomposition products, such as chlorine monoxide, or corrosion products, or the accidental introduction of foreign matter before or during packing.

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TABLE 1
Available chlorine, %

Sample	Mean	Range
A, old	69·1	0·7
B, old	68·8	3·1
B, new	71·2	0·5
C, old	68·0	6·1
C, new	73·2	2·7
D, new	72·2	3·1
E, old	65·3	2·7

Table 2
Bulk density, g/cm³

Sample	Mean	Range
A, old	0·855	0·055
B, old	1·004	0·050
B, new	0·980	0·050
C, old	1·042	0·151
C, new	1·000	0·050
D, new	0·780	0·090
E, old	0·839	0·054

Table 3
Other metals, mean%

Metal	Sample A	Sample B	Sample C	Sample E
Sodium	7·8	6·1	6·2	7·7
Iron	0·013	0·018	0·024	0·025
Magnesium	0·11	0·20	0·18	0·07
Potassium	0·003	0·005	0·004	0·003
Aluminium	0·015	0·027	0·030	0·021

Table 4

Chlorate ion, %

Sample	Old Samples	New Samples
A	3·7	-
B	3·1	1·1
C	3·1	1·3
D	-	0·2
E	6·2	-

Table 5

Self-heating test

Sample	Lowest runaway temp. °C	Time, hours
A, old	110	10
B, new	70	15
B, old	100	5
C, new	70	10
C, old	80	10
D, new	80	6
A, old + 3% water	70	16
A, old + 6% water	70	15
C, new + 3% water	60	14
C, new + 6% water	60	14

Fig.I   Gas evolution from 1 g. at 169°C