Runaway Chemical Reaction at Corden Pharmachem, Cork

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This paper describes a runaway chemical reaction which occurred at Corden Pharma Ltd in Cork on Monday 28th April 2008. The incident resulted in the death of one operator and serious injury to another. The investigation carried out jointly between the Health and Safety Authority and Chilworth showed that the immediate cause of the incident was due to omission of acetone in reactor K6003 prior to Diethylcarbamoyl chloride (DECC) addition during synthesis of the acyloxypyridinium salt precursor to 2-cyano-3-methylpyridine. This resulted in a higher than expected adiabatic temperature rise leading to a two-stage decomposition, firstly of the acyloxypyridinium salt and then of the Picoline-N-oxide starting material. The energy of the event was significant and resulted in considerable distortion of the reactor and release of contents at high temperature and pressure. The pressure wave resulted in significant building damage and ejection of debris. The exact reason why acetone was omitted has never been established although, with such a potentially severe consequence, the investigation concluded that more should have been done to eliminate the possibility of human error for this process step. The investigation also highlighted deficiencies in the sites execution of its process safety management systems, particular its HAZOP / risk assessment for this process. The paper presents the conclusions from the investigation as well as general lessons applicable to the chemical and process industries.

Introduction

Corden Pharma Ltd (trading as Corden Pharmachem) in Cork undertook toll chemical manufacturing. On Monday 28th April 2008 at approximately 01:25 am, a runaway chemical reaction occurred in Production Building no.2 (PB2). The runaway occurred during manufacture of 2-cyano-3-methylpyridine (CMP) and resulted in sufficient distortion to a pressure rated reactor to allow loss of containment, most likely as a high temperature and pressure spray, of a large proportion of the contents. Two operators were present in the building at the time and both received severe injuries. One operator subsequently died from his injuries. Substantial damage also occurred to the building. The incident investigation was led by the Health and Safety Authority (HSA) with technical support from Chilworth Technology Ltd. This joint paper with the HSA describes in detail the events leading to the incident, the consequences and also explains the outcome of the investigation which examined the immediate cause and underlying root causes. A site-wide prohibition notice was served by the HSA on the day of the incident and a number of months after the incident, there was a management decision to close the site.

Incident damage description

Most building damage was on the north side of Building PB2 (Figure 1). Sections of the cladding were completely displaced, with a roller shutter door found on the ground by the drum storage area on the north side (Figure 7). There was debris on the ground extending a considerable distance from the building. Internally, most of the damage was to the 2nd floor and 3rd floor of PB2 with the 2nd floor (where the main part of the reactor that failed was located) sustaining the worst damage (Figure 2). Most of the damage on the 3rd floor was to the roof (Figure 4) caused by the fact that the direction of release was primarily upwards through the reactor solids charge chute (Figure 3). The energy was sufficient to result in cracking to the concrete block walls (Figure 5). In addition to damage consistent with overpressure energy, there were significant black deposits covering much of the equipment, ground and walls on the 2nd and 3rd floors.

Damage to process equipment was mostly confined to K6003 on the 2nd floor with the vessel dished end deforming, significant flange manway distortion, rotation of nozzles (Figure 6) and complete 'blow out' of the manway gasket leaving a gap of about 10 mm through which reactor contents were ejected. The top cover on the Solids Charge Chute was completely torn off from the top of the chute. This required the shearing of four bolts. The cover was found on the ground outside on the south side of the building (Figure 8). The Solids Charge Chute butterfly valve was also sheared off and transported up the Solids Charge Chute. This was found on the 3rd floor (Figure 9).

Figure 1: PB2 north side
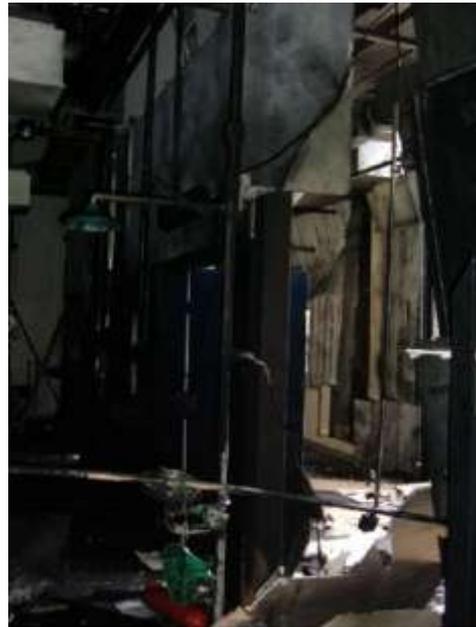
Figure 2: Internal damage

Figure 3: 3rd floor charge chute

Figure 4: 3rd floor roof damage

Figure 5: Cracks in concrete

Figure 6: Nozzle rotation

Figure 7: Roller shutter door

Figure 8: Solids charge chute lid

Figure 9: Butterfly valve

Process equipment

Since the incident occurred in reactor vessel K6003, a basic sketch of K6003 is shown in Figure 7 below with relevant nomenclature. A description follows.
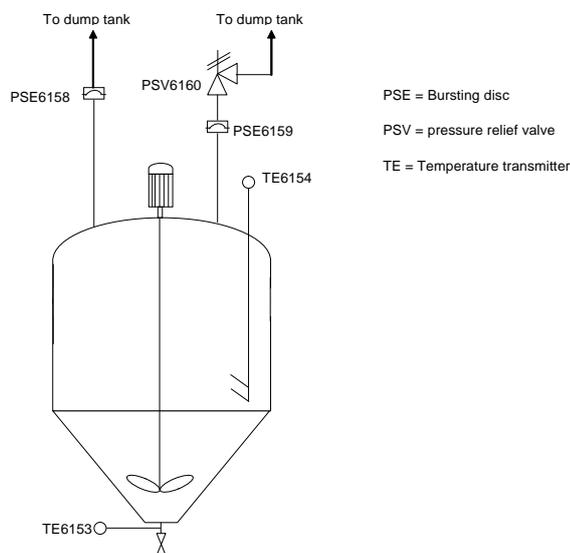

Figure 7: Sketch of key features of K6003

K6003 was a glass lined carbon steel reaction vessel with an operating volume of 2.5 m^3 and a design pressure of 6 barg. The reactor had a bolted manway on top sealed with gasket material and internally, the reactor was agitated. There were two temperature sensors in the reactor with one installed in the base of the reactor (TE6153) in the outlet valve. This was referred to as the 'bottom sump' sensor by Corden Pharma Ltd. The other sensor was installed on the baffle (TE6154) and was referred to as the 'top sump' sensor by Corden Pharma Ltd. K6003 was fitted with a pressure relief system comprising of the following:-

1. A bursting disc and relief valve in series. The relief line was 100 mm in diameter from the reactor but reduced to 50 mm just prior to the bursting disc. The relief valve was a 2x3 valve (50 mm inlet and 75 mm outlet) and the discharge pipe was contracted from its 75 mm outlet to 50 mm soon after the valve exit and then expanded again to 100 mm. PSV 6160 was set at 6 barg which is the same as the reactor design pressure. PSE 6159 was set to burst at 6 barg at 80°C.

2. A parallel relief stream to the above comprising of a 100 mm bursting disc (PSE 6158) and 100 mm line. PSE 6158 was set to burst at 7 barg at 80°C.

Summary of process stages

The key process steps involved in the preparation of the acyloxypyridinium salt in reactor K6003 are summarised below [reference 1]:-

1. Inert vessel with nitrogen using two vacuum swing cycles.

2. Wash vessel with 100 litres of acetone (double sign off needed). After wash acetone transferred to waste tank

3. Charge molten PNO (566 kg target) under vacuum (double sign off needed).

4. Sample PNO for water content (target < 1%).

5. Re-inert the reactor as per step 1 above.

6. Charge 1020 litres of acetone from bulk supply. Double sign off needed for acetone addition + need to record sump volume.

7. Cooled to 15-25°C.

8. Charge 702 kg of DECC from drums using residual vacuum over 45-60 minutes maintaining reactor temperature <40°C with application of cooling to the jacket.

Reaction chemistry and thermochemistry

The first stage of the reaction was carried out in reactor K6003 and involved the reaction of Picoline-N-oxide (PNO) with Diethylcarbamoyl chloride (DECC) in acetone. The resultant intermediate, an acyloxypyridinium salt, was then further reacted with an aqueous solution of Sodium Cyanide in another reactor (K6001) to yield the final product 2-cyano-3-methyl pyridine (CMP). Prior to the incident, there had been a number of screening and calorimetric tests carried out on the reaction with PNO and DECC and on the stability of PNO and the intermediate salt. The data available prior to the incident [reference 2] indicated the following:-

1. Picoline-N-oxide has a detected exothermic onset temperature of 181.7°C which reduces to 161.7°C after applying a typical 20°C safety margin to the Accelerating Rate Calorimeter (ARC) value. This is appreciably above the maximum normal operating temperature. However, the decomposition reaction is observed to be very violent, generating high temperature and pressure and rates of rise.

2. The intermediate salt is thermally unstable and has a detectable onset of 71.5°C in the Phitec II. However, decomposition is also very violent. Although not tested, the dry salt (no acetone) is likely to have a considerably lower onset, and be of greater violence owing to the absence of diluent/heat sink

3. The heat of reaction of the desired reaction is not particularly high although with an adiabatic temperature rise of 41°C and a starting temperature up to 40°C, there is the potential to exceed 71.5°C in the case of an all-in (rapid) reaction or cooling failure. However, with 30% accumulation of DECC, a temperature rise after addition of 12.3°C would be expected which, assuming that the starting temperature was below 40°C as intended, would not allow the reaction mixture to reach 71.5°C.

Based on this information, on paper at least, there should have been knowledge about the hazards of the process.

Investigation into possible causes

The damage to reactor K6003 suggests that internal deflagration[1] was not a likely cause of the incident for the following reasons:-

1. The deflagration pressure of acetone from atmospheric pressure is 7.3 barg [1]**.** The design pressure of the reactor was 6 barg and the test pressure 9 barg. Therefore pressure well in excess of 9 barg would have been needed.

2. The inerting sequence appeared to have been carried out based on DCS outputs salvaged which showed the usual vacuum swing trends. However, whether an inert atmosphere had actually been established could not be confirmed in the absence of oxygen level monitoring.

The pressure was therefore more likely to have been derived from a higher pressure-generating event such as a runaway reaction or decomposition. Under test conditions, the PNO and intermediate salt are capable of generating pressures in excess of 20 barg in the event of decomposition. The cause of the damage to the building indicated the blast wave was directional in nature, possibly more consistent with a physically generated blast wave from vessel failure.

Possible cause of the sudden overpressurisation of K6003

Based on DCS trend data[2] recovered after the incident, it was that in the time leading up to the incident, the temperature was generally below 60°C. This is appreciably below the temperature at which PNO would be expected to start to decompose. However, it was known that the intermediate salt is unstable above 71.5°C although again, at no time was the temperature above 71.5°C just prior to the incident. This indicates that there must have been an error in the process to create an abnormal condition and possible onset of decomposition at a lower temperature. It is possible that incorrect materials could have been added although there was no evidence of anything other than PNO or DECC on the reactor floor. All lines which should have been isolated to the reactor, appeared to have been isolated. In addition, the bulk solvent supply was set up for the intended solvent which is acetone.

The violence of the pressure-generating event which occurred suggests a decomposition reaction. However, for the intermediate salt to decompose, the onset temperature would need to be reduced to below 71.5°C or the adiabatic temperature rise of the reaction would need to be increased to access the decomposition. The most likely cause of this based on existing calorimetric data would be to omit the acetone. DCS trends of a previous 'normal' batch showed that early on, the top and bottom sump temperatures differed. This is because the top sump probe was not covered early in the reaction sequence. This is despite the addition of PNO. After acetone was added, the top and bottom sump temperatures then match well indicating good mixing and coverage of the top sump probe. The temperature then rose depicting the desired reaction exotherm with a final temperature rise coinciding with heat being applied to the jacket to reflux the acetone and complete the reaction.

With the batch involved in the incident, there was poor consistency between the two temperature probe readings until the incident occurs. This suggested that the top probe was not covered properly until just before the incident and one possible cause of this was that the 1020 litre acetone charge had not occurred (i.e. the main acetone charge required just prior to the DECC addition). Further investigation using other DCS trends confirmed that the 1020 litre acetone addition had been omitted. For example, both the acetone flowmeter and acetone tank level gauge trends showed this to be the case. An interview by the Health and Safety Authority with the surviving operator also confirmed that indeed acetone had not been added.

It was clear from DCS trends, that vacuum had been pulled on K6003 just prior to the incident. This vacuum was also evident on the 'normal batch' trend and depicts DECC addition which is carried out under residual vacuum. Other evidence that liquid had been added included observation of DECC drums near the reactor (Figure 10) and agitator torque sensing trends i.e. increased torque due to increased viscosity just after the vacuum was pulled.

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[1] A **deflagration** is a combustion reaction (i.e. explosion) where the flame front travels at below the speed of sound at local conditions.

[2] The DCS trend graphs could not be reproduced in this paper.

Figure 10: DECC drum with reactor feed line inserted

There are a number of reasons why omission of the acetone could have resulted in an exothermic runaway or decomposition when DECC was added:-

1.   The acetone provides a heat sink so the adiabatic temperature rise of the desired reaction would be increased.

2.   The intermediate salt in the absence of solvent would likely have a lower onset temperature for decomposition and decompose more violently.

3.   The temperature of the batch when the DECC was added was higher than usual.

4.   The omission of acetone would have increased the batch viscosity affecting heat transfer and mixing efficiency.

5.   Stratification of the DECC in the absence of acetone may have occurred resulting in a delay in the desired reaction (no longer feed rate controlled) and then a rapid desired reaction (all-in) which lead directly into decomposition.

6.   The absence of acetone would remove the reflux / boiling "barrier" that would ordinarily have eliminated the possibility of heating the batch beyond the boiling point of acetone.

Experimental verification programme

Three tests were carried out – an open glassware mixing study, isothermal reaction calorimetry (using Mettler Toledo RC1*e*) and an adiabatic stability test on the concentrated product (using Accelerated Rate Calorimetry (ARC)). Each is described below.

The glassware experiment was carried out to assess the potential violence of the reaction as a safety precaution before proceeding to other calorimetric studies. It was not intended to be used to gather any specific data to characterise the reaction but did show that the reaction was highly exothermic and became more viscous with amount of DECC added.

The RC1 test was used to determine the heat of reaction of the PNO / DECC reaction with no acetone and 50% of the DECC added. It was also used to produce the intermediate salt for the ARC test. A starting temperature of 44°C was used based on an estimate from the DCS trends of the lowest likely addition temperature. This is higher than the 'normal' start temperature as addition of the acetone normally results in an appreciable temperature drop. The RC1 test results showed that the reaction had a heat of reaction of -53 kJ/mol of DECC added and an adiabatic temperature rise of 92.4 K. There was no accumulation noted and the reaction generated a small quantity of gas (577.4 ml). The reaction started soon after addition of the DECC and the difference in the value of U (overall heat transfer coefficient) at the start and end of reaction was appreciable indicating that the mixture became viscous - consistent with visual observation.

Figure 11 shows the graphical output from the RC1 calorimeter which clearly shows almost instantaneous exothermic behaviour as soon as DECC is added (denoted by the increase in power). It also shows that the power drops off to the base level quickly after all the DECC is added indicating low levels of accumulation at 44°C. Table 1 shows the results of the RC1 test without acetone and compares them to the RC1 results available prior to the incident. The ARC test on the intermediate salt with no acetone showed two clear decomposition exotherms (see Figure 12). The first exotherm started immediately, i.e. at 44°C and reached a peak temperature of 122°C and peak pressure of 18 barg. The second started at about 159°C although peak conditions could not be established because the test had to be stopped through risk of rupturing the ARC test cell. However, the pressure was in excess of 26 barg when the test was stopped. Table 2 compares the ARC test results with previous thermal stability testing available prior to the incident.
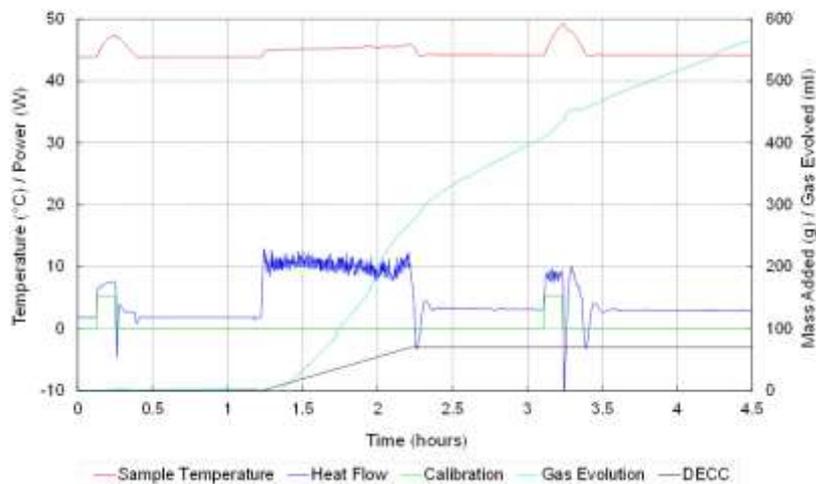
Figure 11: RC1 results for DECC addition at 44°C

Table 1: Comparison of RC1 calorimetry results

| Test	Heat of reaction (KJ/mol of DECC)	Adiabatic temperature rise (K)	Accumulation at end of DECC addition (%)	Gas generation
Previous RC1 (with acetone and all DECC added)	- 32.97	41	30	little
RC1 with no acetone and 50% DECC added	- 53	92.4	0	577.4 ml
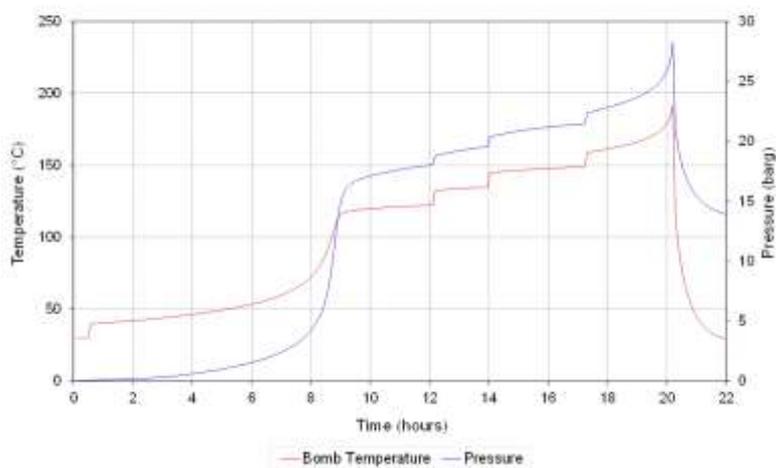
Figure 12: ARC test results on salt / PNO mixture

Table 2: Thermal stability test data for PNO and intermediate salt

Test	Onset temperature (°C)	Max rate of rise	Comments
Phitec on Intermediate salt solution (in acetone)	71.5		Data from Corden [2]
ARC on pure PNO	180	3.4 K/s temperature 408.7 psi/s pressure (ARC bomb then ruptured)	Data from Corden [2]
Carius on pure PNO	150		Data from Corden [2]
ARC on intermediate salt / PNO mix – no acetone	First exotherm from 44°C Second from 159 °C	Not determined due to need to stop test	Results from Chilworth ARC testing

The reaction without acetone is exothermic with a higher heat of reaction and adiabatic rise than the normal process. In addition, the ARC test indicates that without acetone, there is a decomposition reaction starting from 44°C (and likely below). This is likely to be the intermediate salt decomposing. The second decomposition exotherm is likely to be the PNO decomposing and the onset is broadly consistent with previous tests.

It should be noted that the time it takes from the onset to peak conditions from the ARC test cannot be compared directly with that from the full scale reactor for two key reasons:-

1. In the reactor, the PNO / DECC heat of reaction would have quickly raised the temperature of the mixture and hence bypassed the slower reaction rate in the early stages

2. The Phi factor of the full scale reaction will be lower (ARC phi factor is 1.9, full scale probably < 1.5)

The results clearly indicate that without acetone, the intermediate salt would have started to decompose at the starting temperature of DECC addition i.e., almost immediately it formed and built up to a sufficient concentration. The decomposition would have been enhanced by the fact that the PNO/DECC reaction would have raised the temperature higher than expected due to the higher heat of reaction, absence of the acetone heat sink and reduced heat transfer. It is also possible that layering could have occurred resulting in a sudden all-in reaction leading to rapid decomposition. It is also clear that the intermediate salt decomposition could have raised the temperature to the onset of PNO decomposition. The PNO decomposition based upon previous ARC data clearly accelerates to violent levels. As discussed, the timeframe over which the PNO decomposition initiated would likely have been appreciably shorter in the actual reactor.

Were the control measures adequate?

Corden Pharma Ltd had procedures for carrying out HAZOPs[3] and risk assessments. These procedures are highlighted in their Standard Operating Procedures. The procedure for HAZOP listed what constitutes a HAZOP requirement. This included new chemical processes and chemical processes where the existing HAZOP is out of date. The procedures themselves were reasonably comprehensive and required a minimum level of experience / competence of persons leading assessments. A HAZOP was carried out by Corden Pharma Ltd (then Cambrex Cork) between 18/10/2006 and 23/10/2006. Excerpts from the HAZOP report[4] which covered the acetone addition step were examined by the investigation team with a view to understanding to what extent acetone omission as a deviation had been considered.

The examination showed that Corden had identified the deviation 'Flow less' for the acetone addition stage. They had also identified that the consequences could lead to a larger exotherm on DECC addition (which was confirmed by RC1 calorimetry subsequently carried out). However, it was not identified that the large exotherm could lead to the decomposition onset temperature of the intermediate salt being reached (1st decomposition) and subsequently the PNO decomposition point being reached (2nd decomposition). They had also identified that adding a solvent with a higher boiling point could cause a problem i.e. a higher reflux temperature and hence possible onset of self-heating of the intermediate salt. Importantly, what had apparently not been identified (at least in the documents examined) was the deviation 'no acetone'. There are differences of opinion in the HAZOP community as to whether 'less acetone' and 'no acetone' can be considered as equivalent deviations as ultimately the consequences would probably be the same – depending on the extent of "less". However, the causative factors for not adding any acetone at all may be different and hence the necessary safeguards may warrant additional consideration. For example, the reasons for complete omission might include:-

1. No acetone in bulk storage tank

2. Blockage in line

3. Leakage en route from tank to PB2

4. Acetone pump failure

5. Incorrect routing of flexible connections (probably covered under operator error)

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[3] HAZOP = "Hazard and Operability Study"

[4] These cannot be reproduced in this paper

Most of these were not considered, at least not in the HAZOP documentation provided. Totally omitting acetone as opposed to under charge would increase the likelihood of the decomposition conditions being reached, especially as further lowering of the decomposition onset would be expected. With potentially hazardous scenarios such as this, consequence evaluation through adiabatic simulation would have revealed the potential of the deviation, enabling more informed decisions to be made on avoidance and mitigation precautions.

The action that was proposed in the HAZOP to mitigate possible 'Flow less' of acetone was a procedural step i.e. '*add note on approx vol in reactor after addition*' was included in the batch procedure. There was also an instruction to '*Record Approximate sump volume after Acetone addition*' with the expected volume listed as 1550-1600 litres. It was not possible to determine how the operators involved made this estimate, but in the absence of level measurement on K6003 it must have been based on experience of what the correct level looked like through the sight glass e.g. relative to the agitator or using some other 'landmark'. If carried out, this action would at least indicate that the correct amount of liquid was added at that stage, but would not necessarily verify that acetone had been added (the liquid could have been something else). There was a requirement for a second check that acetone had been added (i.e. double sign off procedure). However, for a double sign off procedure to be robust, the independent checker must actually make a thorough check that acetone had actually been added for example by ensuring the pipe routing was correct, that the level in the vessel was correct and a check of the acetone tank level trends on the DCS (and even recording these). The incident indicates that such checks are unlikely to have been carried out or carried out correctly as if they had, the incident should not have occurred.

After the incident, the investigation team found out that the importance of acetone addition was commonly understood. This suggests that it should have been realised that assuring acetone addition in the first place was a safety critical step. However, there was no warning in the batch procedure that this was a safety critical step. Additionally, there was no warning at the reflux stage in the procedure to ensure the acetone does not boil dry or deplete in any way. It only indicates that contents should not be held at reflux for more than 15 minutes. This reflux time was normally controlled / supervised by the operator. Overall, the HAZOP carried out for the CMP process does not appear to have adequately identified key safety critical steps and necessary integrity of the safeguards bearing in mind it was known that the process had high hazard potential. The potential for violent decomposition of the intermediate salt and subsequent decomposition of the PNO was known from calorimetry data available prior to the incident. Therefore it seems reasonable that such a severe consequence through acetone omission should have been foreseen and safeguards of the appropriate integrity determined and implemented.

The integrity of a particular process step should be related to the severity of the consequence. In this case, not only was acetone omission (complete omission) missed as a process deviation in the HAZOP, but the possibility of this leading to a decomposition was not identified (or identified but not documented). No consideration of necessary safeguards to prevent this was therefore given. Because of the known severity of the consequences (based on high rates of pressure rise from the decomposition) and the reliance upon procedures to ensure that the acetone had been added, it would have been good practice to have considered this deviation in more detail. For example, as a minimum, detailed consideration of robust prevention measures should have been given. If these prevention measures were reliant upon operators carrying out tasks then consideration should also have been given to the possibility of human error. For example, the probability of error increases as the complexity of the task increases and at times when operators might be less alert such as during a night shift. It will also depend upon the level of training given to operators. All these factors, and others, would need to be taken into account when deciding how robust the prevention measures would actually be. Because of the suspected severity of the consequences, there would need to be a high level of confidence that the prevention measures were robust under all foreseeable circumstances. Without this confidence, a secondary protection system should have been considered to deal with this deviation e.g. an adequately sized emergency relief system or equivalent. Despite operating, the runaway reaction was clearly not adequately vented by either of the existing emergency vent lines. Details of the relief-sizing basis was not available and retrospective adiabatic calorimetry and DIERS calculations to determine a suitable relief system size for this scenario were not carried out. The relief system itself had some inappropriate design features including:-

1.　Multiple changes in line diameter around the series relief valve and bursting disc. This could result in several chokes and affect relief capacity unless accounted for in design (not verified).

2.　The series relief valve and burst disc set lift pressure and burst pressure respectively were the same (6 barg). The relief valve in a series installation should be set lower to ensure instant opening.

3.　The parallel bursting disc had a burst pressure of 7 barg, above the reactor design pressure.

Despite not being designed for this purpose, the 200 mm diameter solids charge chute, will have provided some pressure relief. In the absence of the solids chute, the incident may have had even more severe consequences by virtue of a more catastrophic vessel failure mode. Another issue that was overlooked was the need for suitable emergency procedures for dealing with loss of control of a reaction. It is understood from the surviving operator that the omission of acetone was realised and the increase in batch temperature was also noticed on the DCS. However, the reaction of the operators was to go to the reactor and isolate the reactor from the overheads equipment (which were mainly glass) to protect them. The operators likely did this with the right intention. However, this action, as opposed to evacuation or even remaining in the control room, cost one of the operators his life. It should have been understood, based on calorimetric data, that omission of acetone would unlikely be unrecoverable once started and so in the absence of a suitable protection system, the response should have been to evacuate. It is always difficult to fully predict how people will behave in an emergency situation but the better they are trained and drilled, the more likely they will take the correct action.

Conclusions

This paper has detailed the investigation into the likely cause of the fatal incident which occurred at Corden Pharma Ltd on 28th April 2008. The following main conclusions could be drawn from the information and evidence available. Much of this information was presented in the prosecution court hearing in 2012.

1. There was conclusive evidence from DCS trends and a key witness statement that the acetone solvent charge was omitted prior to adding DECC to the reactor. The reason for this omission remains unknown.

2. The primary loss of containment was due to excessive pressure in the reactor caused by a runaway reaction. Reaction calorimetry to simulate omission of acetone indicated that that this deviation most likely resulted in exothermic decomposition of the intermediate salt and subsequently the PNO. This resulted in a high reactor internal pressure and damage to the reactor including the manway gasket seal and Solids Charge Chute butterfly valve and end cover plate. Loss of containment of the reactor contents then occurred at both 2nd and 3rd floor levels in Production Building No.2.

3. The level of damage and extent of carbonaceous material deposition outside of the reactor on the 2nd floor could have been caused by the high pressure gas and liquid material suddenly escaping, or due to a secondary explosion on the 2nd floor due to ignition of released reactor contents. The evidence to pinpoint the exact cause of the external damage is not conclusive although the need to know this was secondary compared to establishing the root cause of the runaway reaction.

4. The level of damage and extent of carbonaceous material deposition outside of the reactor on the 3rd floor could have been caused by the high pressure gas and liquid material suddenly escaping from the Solids Charge Chute or again due to a secondary explosion on the 3rd floor due to ignition of released reactor contents.

5. Despite operating, the emergency relief systems for K6003 did not cope with this runaway reaction scenario. However, the 200 mm diameter solids charge chute will have provided some additional emergency relief and possibly even prevented the reactor failing catastrophically.

6. A key root cause of the incident was the failure to fully identify and address acetone omission as a safety critical step in the HAZOP. The consequence of this was to underestimate the risk of acetone omission and incorrectly place reliance upon operator procedure / experience to get this right.

7. The severity of the incident in terms of human loss was influenced considerably by the lack of a suitable procedure for dealing with loss of control of the reaction. The procedure required operators to go to the reactor and shut off valves to the overheads glassware to protect it from pressure. The operators followed this procedure but with potential for a sudden and severe decomposition in the reactor, this required action should have been reviewed. Knowing the timescale and severity of a potential runaway or decomposition following a loss of control situation is important for emergency planning purposes.

Key lessons

There are a number of lessons and messages from the incident that are relevant for anyone undertaking chemical reactions but also for the chemical industry in general. Some key ones are shared below.

1. Runaway chemical reactions can lead to very serious consequences as this and many other past incidents have proven. Pressure rated vessels inevitably fail at a pressure well in excess of their design pressure and so the energy released when they do fail is usually considerable. It is also noteworthy for operating companies to understand that the simple presence of a relief device is not a valid layer of protection, unless that device is adequately sized for the specific worst case scenario. There were a number of deficiencies in the relief line arrangement (including reductions in size, set pressures too high relative to the vessel design pressure, etc).

2. It is important to ensure that thorough reaction hazard assessments are carried out using suitable experimental data to make decisions. In this case, data was available although it appeared not to have been used as extensively as it could have been e.g. in deciding on the required integrity of prevention measures, whether protection was needed e.g. pressure relief to deal with a specific scenario, or in devising a suitable emergency response procedure.

3. When carrying out a HAZOP / risk assessment for potentially hazardous processes, it is very important that the leader of the assessment is suitably competent – and that the overall team membership straddles the full breadth of required chemistry, process, engineering and operating knowledge. Competency cannot be obtained simply by training but requires experience and mentoring to develop.

4. The potential severity of an unplanned event such as a runaway reaction is paramount in determining the suitable integrity of incident prevention measures. In an event of this severity, reliance solely on operator experience to carry out safety critical steps would not be deemed acceptable. In addition, the potential severity of conceivable worst case scenarios should be quantitatively understood (not just hypothetically) such that protection and prevention systems can be developed in proportion to the actual risk.

5. It is very important that identified safety critical steps are clearly identified in operating procedures and that operators carrying out these steps are suitably trained and have clearly demonstrated their competence. Operators should understand the potential severity of the consequences, the basis for safe operation and all the accompanying control measures and the possible outcome of deviating from those measures.

6. When assessing whether reliance upon operating procedures to prevent incidents is acceptable, it is important to assess the human factors elements associated with the tasks in hand. In particular taking into account the increased likelihood of error when carrying out safety critical procedures at times of possible peak tiredness and under lower levels of supervision (e.g. night shifts), is imperative. Where a double sign off requirement exists, the operator and supervisor should understand the reason for this, the consequence of non-compliance, and the specific responsibilities and actions of the sign-off supervisor prior to sign-off. The underlying culture of the organisation – driven by management – should support such procedures.

7. The consequences of incidents such as runaway reactions are not limited to the immediate aftermath. The socio-economic devastation can be far reaching affecting families and livelihoods.

References

1. HSL laboratory report GE/96/02.

2. Carter P. and Rowe S., *2-Cyano-3-methylpyridine Process – Process Safety Testing,* Chilworth report reference J301263R1V1/08 dated 25th July 2008.