

REACTION HAZARD ASSESSMENT AND RISK REDUCTION IN THE CHANGING WORLD OF THE PROCESS INDUSTRIES

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11 brief case studies are used to illustrate different attitudes to, and aspects of, hazard identification and risk reduction in the process industries. Some of these include illustrations of the manner in which specific companies have responded to new legislation. Others involve calorimetry and the hazards associated with exothermic reactions.

KEYWORDS: safety legislation, process hazards, calorimetry, hazard identification, risk reduction

INTRODUCTION

The process industries are facing huge changes: mergers create ever larger companies with centralised facilities, for instance for research and development or for safety testing. Some companies try and become more cost effective by outsourcing many business activities, including R&D and process safety studies: others concentrate parts of their production at lower cost centres such as in China and India. Multi-nationals buy up SMEs, stripping out particular activities of commercial interest and then selling on, or closing down, the remainder. New Directives from the European Union have to be enacted within the Member States, often with varying degrees of both enthusiasm and alacrity.

The process safety consultants who work in the middle of all this change have an unusual and privileged overview of what is happening on different continents, in various countries and in individual companies. They also have an insight as to how companies respond to new legislative demands sometimes with positive results but occasionally with undesirable changes in the way they operate.

A wide variety of brief case studies, a number of which involve calorimetry and reaction engineering, will be used to illustrate specific observations. They include projects undertaken during research and development, during plant commissioning and following accidents and incidents. Some revealed hazards and risks that operators were unaware of whilst others enabled operators to demonstrate to regulatory authorities that their operations were much safer than even they had realised.

CASE STUDY 1: FREEDOM OF INFORMATION AND THE CULTURE OF LITIGATION

A company had a serious accident that resulted in a fatality. Some laboratory experiments were required to try and understand the build up to the accident and to elucidate what might have happened. We were told that all communications regarding these experiments were to be conducted with the lawyers who were acting for the company insurers, rather than directly with any managerial or technical member of staff. This demand created a long and involved chain of communication with many messages going backwards and forwards about scenarios that were to be simulated, recipes to be used, reaction conditions to be chosen, etc. The underlying reason for this, on the face of it, strange demand was that company communications with their lawyers were protected by the principle of client-lawyer confidentiality. However, direct communications (including project reports) passing between the client and their consultants (ourselves) would not be regarded as confidential in a court of law: there could thus have been a requirement to divulge any such information to other parties under the prevailing freedom of information laws. Because the outcome of the experiments was unknown, the insurers felt that this had the potential to undermine their view that the accident could not have been reasonably foreseen.

Observations
Laws about freedom of access to information do not necessarily mean that more information becomes available to the public. When people, or organisations, have information that they wish to suppress, or that they think might need to be suppressed, then they will find ways of doing this. At worst documents and reports will be destroyed: at best they will be written in a more guarded and less open manner. Controversial opinions, or those that indicate a corporate or individual failure will be removed from permanent records (printed documents or their electronic equivalent) and will be communicated in other confidential ways. As a result the "written" word is already becoming devalued and incomplete. A society that thinks that life can be "risk free", and that when something goes wrong there must always be an individual, a corporation or other entity who can be blamed and sued, and a legal profession who are willing to act on their behalf, are partly to blame.

CASE STUDY 2: UNINTENTIONAL CONSEQUENCES OF NEW LEGISLATION

A UK company with significant on-site bulk liquid storage capacity was preparing their COMAH safety report. However they realised that by decommissioning some of their storage capacity they could ensure that they would no longer be classified as a top tier COMAH site: they judged that this would be of significant benefit to them and went ahead with the necessary operating changes to ensure that their classification as a lower tier COMAH site could be fully justified. At first sight this might seem like a wise decision–as has been pointed out many times, a storage tank that you don't have can't leak! But a direct consequence was that the site now required an increased number of tanker deliveries, albeit in smaller quantities: thus rather than sitting in a stationary storage vessel, at a well run site, the chemicals are now spending more time being loaded into IBCs, being driven around the European and UK road network and being unloaded at the client's site. Of course, nobody intended that implementation of the Seveso II Directive (and hence the COMAH regulations) should increase the number of traffic movements of hazardous chemicals within Europe, but that seems to have been a direct consequence. Is this a widespread and significant problem? Is anyone monitoring the frequency of traffic accidents, and tanker and bulk chemical loading and unloading incidents and accidents, pre- and post-Seveso II? What is the cost of these? By way of illustration, on 30th August 2005, at the time that this paper was written, a lorry carrying hydrogen peroxide caught fire and exploded on the M25, completely closing the motorway for two hours in both directions between junctions 11 and 13 and bringing chaos to Britain's busiest motorway. What was the cost to the nation of this single incident?

Observations
The intentions behind new legislation may be laudable but the reactions to it may be unpredictable. In this case the site operator's natural focus was primarily concerned with easing the route to COMAH compliance rather than minimising the societal risks attributable to his activities. Exporting a problem to some other section of the community at large (who may be much less able to deal with it) does not solve the problem!

CASE STUDY 3: EXAMPLES OF BAD LEGISLATION

Despite the painfully long gestation period between European legislation first being conceived and then finally becoming a reality, we still have many examples of poor legislation and/or supporting documentation – flawed, badly written and without accompanying practical examples of the way in which it should be implemented or the type of documentation that the regulatory bodies are expecting operating companies to produce. Frankly, the latter is sometimes the case because the regulatory authorities themselves do not know exactly what they want: and if they don't know then how can the operating companies? Examples of this led to problems with both a high rejection rate and an overly long response time by the HSE for early COMAH Safety Report submissions.

A very specific example of poorly drafted legislation is in the ATEX 137 (Directive 1999/92/EC) which defines an "explosive atmosphere" as "a mixture with air, under atmospheric conditions, of flammable substances in the form of gases, vapours, mists or dusts in which, after ignition has occurred, combustion spreads to the entire unburned mixture". Can mixtures of fuels in oxygen, or chlorine (as opposed to air), not be explosive? And why should the definition be limited to "atmospheric conditions"? If a hydrogenation reactor is being operated at 1.05 bara, but there was a failure to purge the air out of the reactor headspace, then is there no possibility for an explosive atmosphere to be present? This is simply an example of lack of precision in the use of language of which the European Union should be ashamed. Unfortunately this definition of an "explosive atmosphere" has already started to propagate, e.g. into SI 258 in Ireland where it is reproduced word for word. No doubt this is also true in other member states.

Staying with the ATEX Directives, Category 1 or 2 equipment has to be certified by a Notified Body. But if the test methods to certify a particular type of equipment, and the results to be attained, are not yet specified, then how can uniformity of application be expected from all Notified Bodies in every Member State? Many testing standards have been, or currently are being, defined but in the interim the un-level playing field (that this harmonised legislation was meant to eliminate) remains.

Observations
the objectives of legislation should be clear. Precision of language, and translation, is important. Bodies responsible for implementing the new legislation should provide clear guidance and write standard test methods before the new legislation is introduced.

CASE STUDY 4: EXAMPLES OF POOR IMPLEMENTATION OF LEGISLATION

A non-UK company was implementing the ATEX 137 Directive on their large production site. The individuals charged with doing this decided that the best approach was to blanket zone large parts of the site as either zone 1 or zone 2 areas. This made the area classification exercise, and the preparation of the zone drawings, relatively simple. However it immediately created many anomalies: Category 2 and Category 3 equipment (for zones 1 and 2 respectively) had to be installed in many locations where it was clear that flammable atmospheres would not be present – just because the poorly thought out area classification drawings imposed this requirement. In the end there were so many anomalies that a procedure was instituted by which dispensation from the process safety group of the company could be given in specific circumstances for the requirement to install Category 2 (or 3) equipment. Soon the whole system fell into disrepute and a more legitimate area classification exercise then had to be undertaken.

A similar example involved a conventional laboratory that contained a small inventory of flammable substances. The decision was made by the operating company to classify the whole of the laboratory as a zone 2 area, thus requiring that only Category 3 equipment should be present. This, of course, was completely impractical – try buying Category 3 laboratory balances, analytical equipment, heater/chillers, hotplates, stirring systems, water baths or the many other items of ordinary equipment that are ubiquitous in laboratories. And what about the implications for the laboratory heating and lighting systems, or for the supply of electrical power? The blanket zone 2 classification was in this circumstance inappropriate. It would have been much more sensible to restrict the locations within the laboratory at which certain types of work could be undertaken, i.e. those activities with higher risks of generating a flammable atmosphere of significant volume, and then to apply the correct zoning to those areas. In this context the role of fume cupboards dedicated to certain types of activity is obvious. There has been so much confusion about appropriate hazardous area classification in laboratories that the HSE planned to issue specific advice on this topic, see Tyldesley (2003). At one stage this, or a draft of it, did exist, HSE (2004), however at the time of writing this no longer seems to be available.

Observations
short cuts and quick fix solutions, without looking at the bigger picture, rarely bring lasting benefit. Getting it right first time (i.e. in this case the area classification) is usually the best, and in the long term cheapest, policy.

CASE STUDY 5: PROCESS SAFETY STUDIES TOO LATE IN THE PROCESS DEVELOPMENT TIMELINE

A new reactor for batch and semi-batch operations was in the process of being commissioned. At a very late stage, far too late, a HAZOP team was meeting. One member questioned how it was known that the reaction inhibition system would be effective in halting a runaway reaction. The chemists present viewed this as a rather naïve comment: they clearly thought that everyone should know that the addition of caustic would stop the reaction immediately. The questioner persisted: where was the proof that the caustic solution would kill the runaway? In a great hurry we were asked to carry out the runaway reaction experimentally and at specific conditions to inject the caustic in order to demonstrate once and for all that the caustic was effective as a reaction inhibitor. It was not! The experiment proved that, yes, the caustic addition slowed the reaction down and thereby bought a bit of additional time to tackle the problem. However after a relatively short period the reaction rate accelerated again with the runaway becoming very violent and much more severe than it would have been if the caustic had not been added.

Observations

When others belittle your lack of knowledge be willing to stand your corner unless they can demonstrate that what they say is correct. Hearsay is not a sufficient basis on which to make safety critical decisions. Can you demonstrate that your assumptions and conclusions are correct?

CASE STUDY 6: AN EXAMPLE OF HOW TO INCORPORATE SAFETY INTO THE PROCESS DESIGN

A. ELIMINATING HAZARDS FROM PROCESS DESIGN

At a very early stage of process design a prudent research chemist sent a sample of a distillation residue for thermal stability screening. At temperatures that actually overlapped with those used during the batch distillation there was detectable exothermic activity. Under adiabatic conditions this developed into a violent runaway reaction with associated rapid generation of very large quantities of non-condensable gas. Attempts to improve the synthesis route so as to eliminate the formation of the by-product that was concentrated in this distillation residue failed. However, all was not lost for when alternative separation techniques were considered fractional crystallisation at low temperature proved to be particularly effective. As a result the risk of the thermal decomposition of the unwanted by-product could be removed entirely as a credible operating hazard.

B. INCORPORATING KNOWN HAZARDS INTO THE PROCESS DESIGN

A few years ago a large multi-national pharmaceutical company was scaling up a new process. One of the very late stage process safety studies revealed an unexpected but significant thermal instability issue with one of the intermediate reaction products. Unfortunately the results from this one test were not reproducible, but nonetheless they could not be ignored. The final product was of significant economic importance to the company and, for several reasons, late stage major changes in the synthetic bond forming sequence were not easy to make. As a result the plant had to be operated with the knowledge that loss of temperature control at this one particular stage could lead to a significant exothermic runaway event. The risks of this were reduced to an acceptably low level by a combination of procedural changes to the standing process instructions, by reducing the maximum possible temperature of the heating medium and by a number of plant design changes including the introduction of high integrity trips and interlocks.

C. KEEPING THE PROCESSING SIMPLE

A surface coatings manufacturer was in the habit of adding an initiator to a monomer in a mixing tank and then pumping the mixture to a batch reactor. The reactants were then allowed to self-heat up to a defined temperature at which point the cooling was turned on and the temperature was held constant. One day there was an unforeseen hold up in the transfer of the pre-mixed solution and a runaway reaction occurred in the mixing tank which had no cooling capability. After the incident it was realised that this mixing duty could be carried out more safely within the reactor itself and the need for the mixing tank was eliminated. Later still R&D studies demonstrated that an equally good product could be made by running the process in a semi-batch manner. A balance was struck between the reaction temperature and the feed rate such that the enthalpy "accumulation" associated with the build up within the reactor of a significant concentration of unreacted, or partially reacted, monomer was kept to a low level. The potential for a significant runaway reaction on loss of cooling during normal operations was thereby eliminated.

Observations

Lessons learned: Identifying and understanding the process hazards at an *early* stage of process design can enable the hazard to be removed or circumvented. This leads to a process with a greater measure of inherent safety. Conversely, learning about the hazards too late in the cycle of process design can mean that the in-built hazard has to be accepted. In example B the basis of safety for running the process had to involve robust procedures that ensured that, although the hazard was present, the risks associated with it were at all times acceptably low. Thinking "outside of the conventional box" can sometimes lead to simpler and safer process plant and procedures.

CASE STUDY 7: DON'T BE AFRAID TO CLAIM THAT YOUR PROCESS IS, IN SOME RESPECTS, INHERENTLY SAFETY

A mainland European company was in discussion with its local enforcement agency about its reactor emergency relief vents. The company accepted that the vents had to be capable of maintaining an adequately low pressure during their "worst credible maloperation" (widely perceived to be a runaway reaction) but were unable to demonstrate that the vents were in fact large enough for this duty. They had no thermokinetic information on their normal processes, let alone for their worst credible maloperations, so a first step was to obtain isothermal calorimetry data for their desired operation. The process involved sparging a gaseous reagent into a mixture of liquid reactants over 4 hours: under normal conditions the reaction was shown to be essentially feed rate limited with an enthalpy "accumulation" of $<1.5\%$: this corresponded to an adiabatic temperature rise of only $\sim 3^{\circ}C$. If the liquid reactants were at too low a temperature then the gaseous component would react more slowly and the reactor head space pressure could rise. In this case a high integrity trip would isolate the feed. Under these conditions the total inventory of reacting gas in the headspace would still be less than that dissolved in the liquid phase at the correct operating temperature. If the 1.5 barg bursting disk fitted to the reactor did rupture then the reaction would be quickly arrested as the concentration of the gaseous reactant fell to zero. With the reaction being carried out significantly below the atmospheric boiling temperature of the most volatile species in the reactor, the company was able to argue that there was no potential for over-pressurisation of the reactor due to a runaway reaction. In this case the venting could be sized for other candidate duties such as over-pressurisation from an upstream source, fire relief, etc. At first the company was worried that the regulatory authorities would be unlikely to accept this line of argument and at one stage they asked us if we could identify a legitimate and more demanding runaway scenario but for which the existing pressure relief system was just adequate! Happily the enforcement authority was more enlightened than the client anticipated and they accepted the evidence that a worst credible runaway reaction scenario could not over-pressurise the reactor.

Observations

Complete inherent safety is seldom, if ever, attainable, but it should always be the ideal goal for which the process designer strives. If you have a reaction process with inherently safe features then discuss and explain the reason behind your claim and produce the evidence to demonstrate that what you say is correct. Don't feel compelled to accept every demand made by the regulatory authority, certainly not initially!

CASE STUDY 8: IF YOU HAVE CENTRALISED SERVICES THEN MAKE SURE THEY ARE GOOD AND SET UP IN SUCH A WAY THAT STAFF WANT TO USE THEM

It is not unusual for a client to ask us to undertake work that we know can be provided by internal services within their own organisation. Our normal policy is to point this out to them. Some of the frequent reasons that we hear from individuals who do not want to make use of these in-house service are:

- The service is too slow and the timescale for delivery of results is unacceptable, or is too variable.
- The service is too expensive.

- The report that they will receive is written by experts (for experts?) and they can't understand it.
- They want an independent opinion.

Conversely we are sometimes contacted by the in-house service itself who wish to sub-contract some of their workload, perhaps because they need access to specialist equipment or because they need help to reduce their backlog of work. Their perception of the service that they provide to colleagues is almost always very different from that expressed above, e.g. that (because of company policy) their services are too cheap (or even free to the end user) with the result that everybody commissions all sorts of testing without really thinking about whether all of it is really useful or necessary!

Observations
Cost internal services sensibly, cheap enough to encourage their use but expensive enough (even if still subsidised) to make people realise their true cost. Whenever you write a report think who it is being written for. Always write reports for the reader, never the author nor to try and impress others! Real experts can communicate in simple, jargon free, language. Deliver services in a timely manner.

CASE STUDY 9: DEVELOP ROBUST, ERROR TOLERANT PROCESSES

A semi-batch chemical production had been run for several years without incident, Partington (2002). Then, suddenly on an otherwise quiet Sunday morning, and with very little warning, the top lid, agitator and gearbox were blown off a 2.3 m^3 reactor: consequential damage to buildings and equipment was very significant though luckily nobody was injured. The direct cost of the incident was ~£2.7 million.

Well designed processes should be robust (error tolerant), i.e. so that a significant incident will never be the consequence of reasonably foreseeable errors (e.g. in recipe quantities, order of addition, addition rate, mixing problems, loss of cooling, temperature being out of range, etc.) With this process a low temperature could lead to a very significant build up of unreacted feed and a high temperature could rapidly lead to a reaction enthalpy release rate that was beyond the reactor cooling capacity. Although the process had been run safely for years it relied heavily on correct manual control and the process was not robust to operator errors (e.g. when trying to maintain the right process temperature) or equipment faults (e.g. such as a fouled heat exchange system or a leaking steam valve).

Observations
Specify what process errors can reasonably be expected and confirm through appropriate small scale experiments that the process is tolerant of these errors. Recognise that operator error should be expected with plant and control systems that require manually intensive operations. Through appropriate maintenance and inspection regimes confirm that plant

services do not become compromised (e.g. by fouling of heat transfer surfaces or because of a passing valve.)

CASE STUDY 10: ONE PURPOSE OF EXPERIMENTS IS TO REVEAL THE UNEXPECTED

A process involved sparging a gaseous reagent into a liquid reactant mixture. The worst credible scenario was that one liquid component was omitted but was then added rapidly to the remaining components after they had already been saturated with gas. It was hoped that the potential for a runaway reaction would be limited and that the existing reactor pressure relief system would be adequately sized for the exothermic runaway that could result. The logic behind this view was that the solubility of the gas would be too low to provide a significant reservoir of the gaseous reactant. This in turn would mean that the runaway potential was limited. The results from a test in a low phi-factor adiabatic calorimeter surprised all those who held this viewpoint. A temperature rise of over 180°C in ~15 seconds was observed with a peak heat-rate in excess of 1380°C min^{-1}.

Observations

Gut feelings and intuition are not always reliable predictors of actual chemical behaviour, even if their author is experienced and knowledgeable. If key plant design features and safety critical systems depend on such foundations then their validity must be independently verified, e.g. by an appropriately scaled experiment. Experimental studies often reveal weaknesses in the ability to predict, or to model, how chemical systems will behave in unusual circumstances.

CASE STUDY 11: MANAGEMENT OF CHANGE

A. THERMAL INCINERATORS

Discharge limits of VOCs to air under current legislation are now rightly required to be at much lower limits than was previously deemed acceptable. In this context some companies have installed "end of pipe" treatment in the form of a thermal incinerator, often sourcing their plant from one of several specialist suppliers. However, failure to anticipate fully the ranges of cyclic VOC load in the inlet ducting to the incinerator has lead to a number of incidents when flammable atmospheres have been ignited with consequent fires and/or explosions.

B. SEWAGE DISPOSAL

Following legislation that banned the dumping of sewage sludge at sea, water companies have started to dry sewage sludge and to market the product as a fertilizer or fuel. In 2001 there were reported to be approximately 110 such sewage drying plants in Europe. In the four years between 1997 and 2001 six significant fire and explosion incidents occurred in the UK in such drying plants due largely to a failure to appreciate the flammable nature of the materials being produced and a poor understanding of the risks involved, Manchester (2001).

Observations
When seeking to achieve one desirable objective don't be blind to other undesirable consequences of your actions. In these cases the management of change initiated by environmental legislation should have incorporated assessments of whether the change could increase the frequency of the formation of a flammable atmosphere, or introduce additional potential sources of ignition. In both cases the desirable objective of reducing emissions (to air or sea) led to an unacceptable increase in the risk of fires and explosions. This was not identified clearly enough at the time the process changes were made.

CONCLUSIONS

Consultants become aware of many industrial practices, mostly good, but sometimes bad. Those companies adopting some bad practices almost always do this out of professional ignorance rather than malice: however laziness and financial restraints are also not unknown! The purpose of this paper is to share some examples of both good and bad practices. The "observations" at the end of each case study summarise some of the main conclusions and lessons that can be learned.

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