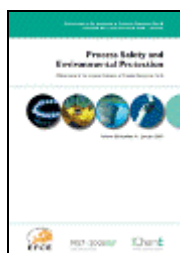


# **Process Safety and Environmental Protection**

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## **Special Issue: Centenary of the Health and Safety Laboratory**



**G. Atkinson, L. Cusco. *Buncefield : a violent, episodic vapour cloud explosion*. Pages 360-370.**

Damage caused by the 2005 Buncefield explosion indicates pressures in excess of 2000 mbar over all of the area covered by the vapour cloud. Such high overpressures are normally associated with high (super-sonic) rates of flame spread. On the other hand, evidence from witnesses, building damage analysis and CCTV cameras all suggest the average rate of progress of the explosion flame front was only around 150 m/s. The high overpressures in the cloud and low average rate of flame advance can be reconciled if the rate of flame advance was episodic, with periods of very rapid combustion being punctuated by pauses when the flame advanced very slowly. The widespread high overpressures were caused by the rapid phases of combustion; the low average speed of advance was caused by the pauses. Mechanisms of flame spread through radiative ignition of particulates ahead of the flame front provide possible explanations for such unusual episodic behaviour. The first part of this paper reviews a wide range of empirical evidence on average flame speed and rate of blast pressure increase. The second part explores the theoretical consequences of forward radiation and how the new theory might be developed into a practical means of assessment. **Highlights:** ► We review of evidence on average flame speed and rate of blast pressure increase in the Buncefield explosion. ► High overpressures and low average rate of flame advance can be reconciled if the rate of flame advance was episodic. ► Flame spread through radiative ignition ahead of the flame front provide a possible mechanism. ► We consider how the new theory might be developed into a practical means of assessment.

- **Keywords:** Vapour cloud explosion; Overpressure; Particulates; Buncefield

**S. Coldrick, S.E. Gant, G.T. Atkinson, R. Dakin. *Factors affecting vapour production in large scale evaporating liquid cascades*. Pages 371-381.**

This paper presents a computational fluid dynamics (CFD) model of the evaporating liquid cascade produced in a large hydrocarbon storage tank overfilling incident. The model is first validated against the results of a unique series of full-scale experiments, in which

liquid hexane was released from a 10 m high tower. Comparisons are presented for the temperature of both the liquid and vapour in the cascade, and the temperature of the vapour current. The validated model is then used to investigate the effects of different tank bund configurations, and the influence of an accumulating vapour layer on the vapour production process. **Highlights:** ► A CFD model for predicting vapour production from flammable liquid cascades is developed. ► The model is validated against a unique series of large scale experiments. ► Different cascade configurations beyond the experimental range are investigated.

- **Keywords:** Tank overfilling; Cascade; CFD; Source model; Buncefield

**Graham Atkinson. *Blast damage to storage tanks and steel clad buildings.* Pages 382-390.**

The 2005 Buncefield vapour cloud explosion showed the huge cost associated with blast damage to commercial property surrounding a major explosion incident. In most cases there was serious disruption to business activity; in many cases the buildings had to be demolished or abandoned for long periods until extensive repairs were carried out. Another key feature of this and other recent vapour cloud explosions has been the damage done to storage tanks. The blasts almost invariably cause immediate top and bund fires in any tanks surrounded by the vapour – even if they contain relatively high flashpoint materials such as diesel. The first part of this paper describes the patterns of damage observed in buildings in the industrial estates around Buncefield. Methods for assessing the degree of external and internal damage are presented. The second part of the paper deals with failure modes and ignition of various types of liquid storage tank during vapour cloud explosions. Again, the Buncefield data provides excellent examples that illustrate the importance of tank design, fill level, location relative to the cloud, etc. **Highlights:** ► Evidence on damage to tanks and buildings at the Buncefield explosion. ► Large portal frame structures are vulnerable to pressures of order 1 kPa. ► Slow build up of pressure leads to a single large vent in one side. Other sides then see reduced pressures. ► Blast penetration into vented buildings is analysed. ► Blasts cause fires in any tanks surrounded by vapour.

- **Keywords:** Blast damage; Vapour cloud explosion; Steel building; Storage tank; Buncefield

**S.E. Gant, G.T. Atkinson. *Dispersion of the vapour cloud in the Buncefield Incident.* Pages 391-403.**

Dispersion of the flammable vapour cloud in the 2005 Buncefield Incident is examined. Footage from security cameras around the site is analysed and the results from Computational Fluid Dynamics (CFD) simulations of the vapour dispersion are presented. It is shown that the shape of the terrain and the presence of obstacles significantly affected the dispersion of vapour from the overflowing tank. The CFD model is shown to produce similar qualitative behaviour to that observed in the incident, both in terms of the arrival time of the vapour cloud and its final depth. **Highlights:** ► The dispersion of the vapour cloud produced in the Buncefield Incident is examined. ► Images of the visible mist from security camera records are analysed. ► CFD simulations of dense gas dispersion are presented and compared to observations. ► Cloud behaviour is shown to be affected significantly by terrain and obstacles.

- **Keywords:** Buncefield; Dense gas dispersion; CFD; Terrain; Obstacles

**Diego Lisbona, Joseph Januszewski, Helen Balmforth, Mike Wardman. *Societal risk assessment of major hazard installations using QuickRisk.* Pages 404-414.**

QuickRisk is a quantitative risk assessment tool developed at the Health and Safety Laboratory for use in assessing societal risk around onshore major hazard installations to inform land-use planning decisions. It uses release scenario information, parameterised consequence models, weather data, and population data from the National Population Database (NPD). This paper describes enhancements to the NPD methodology to include workplace populations. It describes the novel numerical, graphical and geographical representations of societal risk produced by QuickRisk. F–N data are analysed in terms of scenario FN curves and Delta PLL vs. N curves, where PLL is potential loss of life. The Delta PLL curves could be useful for comparison of FN curves against FN criterion lines or other FN data on a PLL basis. Geographical representations generated from PLL density maps show: the distribution of PLL dominating release scenarios or the percentage of risk contributed by the PLL-dominant release scenario, the maximum number of fatalities associated with the worst-case event, and the associated release scenario. Geographical representations are also generated of the maximum population that would meet a PLL density criterion, and the relative population change that would match a given PLL density criterion. These novel representations of societal risk could be useful for more effective communication between stakeholders on the risk levels in the vicinity of major hazard installations. **Highlights:** ► Novel representations of societal risk have been developed. ► Graphical representations include Delta PLL curves, which facilitate comparisons between FN curves and risk criteria. ► Geographical representations of societal such as ‘risk-informed population density maps’ have been developed. ► ‘Risk-informed population density maps’ show population densities that would bring the PLL above a pre-defined criterion. ► Geographical representation of scenario rankings based on PLL and the maximum number of potential fatalities are presented.

- **Keywords:** Societal risk; QuickRisk; Major hazards; National population database; NPD; Land-use planning; QRA

**Helen A. Cruse, Jonathan E.H. Buston, Luc N. Véchet, Graham A. Tickle, Ralph Rowlands. *Modelling spills of water-reactive chemicals*. Pages 415-423.**

This paper describes part of a programme of work undertaken at the Health and Safety Laboratory (HSL) to investigate the behaviour of selected water-reactive chemicals. Following an accidental release, such substances react exothermically with any water present, generating acidic vapours. The STAWaRS (Source Term Assessment of Water Reactive Substances) software was developed for the Health and Safety Executive (HSE) by ESR Technology to model this complex process. The aims of the study described here were to provide experimental validation of the heats of hydrolysis used within STAWaRS, and to perform sensitivity studies on selected STAWaRS input parameters. The heat of hydrolysis of acetyl chloride was measured and showed good correlation with the value used within STAWaRS. Some of the variables that influence the severity of acetyl chloride spills are examined, with reference to predictions made by the STAWaRS model. The heats of hydrolysis of titanium tetrachloride previously measured at HSL are also discussed, and the effect of adopting these experimentally derived values for modelling spills is shown for a hypothetical land use planning case. This study demonstrates the importance of using experimentally validated values for STAWaRS input parameters. **Highlights:** ► HSL is involved in experimental and theoretical studies of water-reactive chemicals. ► STAWaRS is a new source-term model for spillages of water-reactive substances. ► The surface water depth and heat of hydrolysis are key model input parameters. ► Experimental values of the heat of hydrolysis of acetyl chloride are presented. ► The role of STAWaRS in land use planning assessments is discussed.

- **Keywords:** Water-reactive chemical; Spill; Acetyl chloride; Titanium tetrachloride; Consequence modelling; Land use planning

**Stephen R. Graham, Robert Hodgson, Luc Vechot, M. Iqbal Essa. *Calorimetric studies on the thermal stability of methyl ethyl ketone peroxide (MEKP) formulations. Pages 424-433.***

The energetic decomposition of methyl ethyl ketone peroxide (MEKP) and its formulations have long been known to present a significant risk. Indeed, MEKP has the highest number of reported decomposition incidents of all organic peroxides, many of which have led to significant numbers of fatalities, injuries and damage. It is noteworthy that incidents have been reported at all stages of the product lifecycle. This paper is derived from incident-investigation work and provides a summary of serious incidents involving MEKP, followed by details of calorimetric experiments performed to investigate thermal stability of representative MEKP formulations containing varying amounts of MEKP monomer. In particular we report the wide degree of variation that exists between commercial MEKP formulations, even between materials that are of the same nominal formulation. Such variations are detectable using differential scanning calorimetry (DSC). Follow-up studies performed on a representative MEKP formulation containing MEKP monomer indicate that a risk of decomposition exists at temperatures well below the reported self-accelerating decomposition temperature (SADT) of the products. As such, the experimental results reported here suggest that lower storage temperatures (commonly recommended by manufacturers to maximise shelf life) should be considered as being essential throughout the product lifecycle to reduce the risk of accidents in storage and transportation. **Highlights:** ► Decomposition of methyl ethyl ketone peroxide (MEKP) and its formulations. ► Summary of serious incidents involving MEKP. ► Calorimetric investigation into thermal stability of representative MEKP formulations. ► Discussion on suitable storage temperatures for MEKP formulations.

- **Keywords:** Methyl ethyl ketone peroxide; Thermal decomposition; Calorimetry; DSC; ARC; Adiabatic calorimetry

**Diego Lisbona, Timothy Snee. *A review of hazards associated with primary lithium and lithium-ion batteries. Pages 434-442.***

Primary lithium batteries contain hazardous materials such as lithium metal and flammable solvents, which can lead to exothermic activity and runaway reactions above a defined temperature. Lithium-ion batteries operating outside the safe envelope can also lead to formation of lithium metal and thermal runaway. Despite protection by battery safety mechanisms, fires originating from primary lithium and lithium-ion batteries are a relatively frequent occurrence. This paper reviews the hazards associated with primary lithium and lithium-ion cells, with an emphasis on the role played by chemistry at individual cell level. Safety mechanisms to prevent the occurrence and limit the consequences of incidents are reviewed, together with safety tests to monitor compliance with battery safety regulations and standards. Incident information from news accounts and open literature sources are reviewed to extract causal information. It is concluded that the potential severity of incidents during storage, transport and recycling of waste batteries can be significantly higher than in end-use applications. Safe storage, packaging and labelling practices, as well as communication among the parties involved, are essential to ensure safety across the battery lifecycle. It is recommended that a database of lithium battery incidents would be valuable to improve the evidence base for informing accident prevention measures. **Highlights:** ► This paper reviews the hazards associated with primary lithium and lithium-ion cells. ► Safety tests and mechanisms to prevent the occurrence and limit the consequences of incidents are reviewed. ► Incident information from news accounts and open literature sources were reviewed to extract causal information. ► The severity of incidents during storage and recycling of waste batteries can be higher than in end-use applications. ► A database of lithium battery incidents would improve the evidence base for informing accident prevention measures.

- **Keywords:** Primary lithium; Lithium-ion; Battery; Thermal runaway; Fire hazard; Lithium battery fires

**Chrysanthi Lekka, Caroline Sugden. *The successes and challenges of implementing high reliability principles : a case study of a UK oil refinery.* Pages 443-451.**

Research conducted on organisations that are able to sustain excellent safety records over long time periods suggests that there are a number of practices that organisations can adopt to achieve high levels of reliability and safety. These practices are often discussed in the context of major incidents to highlight the safety standards that high hazard organisations should try to emulate. However, previous research has predominantly focused on non-profit organisations, and comparatively little research has examined whether high reliability practices may be meaningfully applied to commercial contexts. This paper addresses this gap by using a qualitative approach to explore the types of reliability-enhancing practices implemented in a UK-based oil refinery in its attempt to achieve its ethos of 'safe and reliable operations'. The findings illustrate the successful application of reliability-enhancing practices in several domains, including: hazard identification and control; emergency preparedness and collection; and analysis of incidents and near misses. Management commitment to safety emerged as an important factor underpinning the successful implementation of reliability-enhancing practices, highlighting its potential significance in the context of commercial organisations. However, promoting an open reporting culture and maintaining high levels of management visibility may be some of the challenges encountered by organisations striving to implement reliability-enhancing practices. **Highlights:** ► We examine the implementation of high reliability practices in a UK oil refinery. ► Good practices implemented for training, incident analysis and hazard control. ► Management commitment and resources are crucial for successful implementation. ► Open incident reporting and maintaining management visibility are challenging.

- **Keywords:** Safety; Reliability; Major hazards; Resilience

**Mark Royle, Deborah Willoughby. *The safety of the future hydrogen economy.* Pages 452-462.**

Limited operating experience with hydrogen energy systems in consumer environments is recognised as a significant barrier to the implementation of the required infrastructure. Significant international effort has been initiated to develop relevant codes and standards. To prevent emerging codes, standards and local regulations from being unnecessarily restrictive, real operating experience is needed using full-scale experimental trials. This paper begins with an overview of experimental work commissioned by both the regulator and industry to help quantify the hazards and risks. It then summarises work co-funded by the GB regulator and EU on: •Jet releases, barriers to reduce safety distances and self ignition undertaken using high pressure hydrogen compression, storage and release equipment; •Liquid hydrogen spills from a road tanker through a vacuum insulated transfer hose. Findings include: jets are predominantly momentum-driven; a 60° barrier reflects less heat back to the source than a 90° barrier; the lowest burst pressure for self-ignition is 3.55 MPa; and initial findings suggest a pool can be formed if a liquid release is made onto the ground. The experimental data from this work has been used to establish safety distances, and define conditions under which self-ignition may occur.

- **Keywords:** Hydrogen; Self-ignition; Liquid hydrogen; Hydrogen safety

**Jill Wilday, Nicola Paltrinieri, Regis Farret, Jerome Hebrard, Leo Breedveld. *Addressing emerging risks using carbon capture and storage as an example.* Pages 463-471.**

The European iNTeg-Risk project is a large-scale integrated project aimed at improving the management of emerging risks related to new technologies in European industry. The project aims to build a new management paradigm for emerging risks as a set of principles supported by a common language, agreed tools and methods, and key performance indicators, all integrated into a single framework. It is using a number of Emerging Risk Representative Applications (ERRAs), or case studies, to inform the development of the framework; one of which concerns the carbon capture and storage (CCS) process. This paper describes the iNTeg-Risk CCS ERRA. Relevant hazards and properties of carbon dioxide are described and the emerging risks from CCS are discussed. Three new tools have been developed or trialled within the ERRA. These are: the DyPASI methodology for taking account of atypical (not usually identified) events during hazard identification; a methodology for including the time dimension in a risk assessment; and life-cycle approaches for risk management and communication. For CCS, the risk assessment needs to include both short-term potential accidents from capture, transport or injection, as well as very long-term risks from storage. Knowledge gaps which are generic to emerging risks are also identified. **Highlights:** ► Emerging risk issues from CCS were defined. ► The DyPASI HAZID methodology for identifying atypical events was successfully trialled. ► A method was developed to take account of the time dimension in risk assessment. ► Life cycle approaches have been applied to CCS. ► Results and knowledge gaps have been generalized to other emerging risks.

- **Keywords:** Emerging risk; CCS; Bow-tie; Time dimension; Life-cycle analysis

**S.E. Gant, M.R. Pursell, C.J. Lea, J. Fletcher, W. Rattigan, A.M. Thyer, S. Connolly. *Flammability of hydrocarbon and carbon dioxide mixtures.* Pages 472-481.**

The effect of carbon dioxide (CO<sub>2</sub>) concentration on the ignition behaviour of hydrocarbon and CO<sub>2</sub> gas mixtures is examined in both jets and confined explosions. Results from explosion tests are presented using a 20 l explosion sphere and an 8 m long section of 1.04 m diameter pipeline. Experiments to assess the flame stability and ignition probability in free-jets are reported for a range of different release velocities. An empirically-based flammability factor model for free-jets is also presented and results are compared to ignition probability measurements previously reported in the literature and those resulting from the present tests. The results help to understand how CO<sub>2</sub> changes the severity of fires and explosions resulting from hydrocarbon releases. They also demonstrate that it is possible to ignite gas mixtures when the mean concentration is outside the flammable range. This information may be useful for risk assessments of offshore platforms involved in carbon sequestration or enhanced oil recovery, or in assessing the hazards posed by poorly-inerted hydrocarbon processing plant. **Highlights:** ► Explosion measurements are reported for methane, CO<sub>2</sub> and air mixtures. ► Ignition of jet releases of methane and CO<sub>2</sub> mixtures in air is examined. ► A new flammability model for free jets gives good agreement with previous data. ► Ignition probability in jets found to be sensitive to disturbances from wind.

- **Keywords:** Flammability; Ignition; Hydrocarbon; Carbon dioxide; Jets; Confined explosions

**Jill Wilday, Mike Wardman, Michael Johnson, Mike Haines. *Hazards from carbon dioxide capture, transport and storage.* Pages 482-491.**

Carbon capture and storage (CCS) is a developing technology which raises a number of issues in terms of safety. CCS involves a chain of processes comprising capture of carbon dioxide, transport and injection into underground storage. In work carried out for the IEA Greenhouse Gas R&D Programme, a number of high-level hazard identification (HAZID) studies have been performed with the help of industry experts. The HAZIDs considered a carbon capture and storage chain involving capture, pipeline transport and injection. HAZID has been performed at a high-level for such a CCS chain with three types of capture technology and using pipeline transport. It is hoped that the results of the HAZID studies will be of use to those carrying out CCS projects, but should not be a substitute for them carrying out a full suite of integrated hazard management processes. A number of example hazards have been described to raise awareness of the range of hazards in a CCS process and to identify barriers which could prevent, minimise, control or mitigate CCS hazards. Bow-tie diagrams have been produced to record the information from this study and to organise it in a systematic way so that it is far less likely that contributors to and mitigators of hazards will be missed. The diagrams are available in Excel spreadsheet format so that they can be used as the starting point for development by specific CCS projects. CCS technology is still advancing and a number of knowledge gaps in terms of safety have been identified which require further development. **Highlights:**

- ▶ Potential hazards from the new technology of carbon capture and storage (CCS) have been identified.
- ▶ The CCS chain including capture, pipeline transport and injection into storage are covered.
- ▶ Hazards are organized in a bow-tie diagram to help identify and address these hazards.
- ▶ Knowledge gaps are identified.

- **Keywords:** CCS; Carbon dioxide; HAZID; Bow-tie; Capture; Pipeline