Environment, Health and Safety Committee

Note On

INHERENTLY SAFER CHEMICAL PROCESSES

The EHSC Note on "Safety Issues in the Scale Up of Chemical Reactions", published the Royal Society of Chemistry, outlines the main options for the safe operation of chemical plant. The first option was to use inherently safer methods. The Royal Society of Chemistry believes that inherent safety is an important issue of which all chemists should be aware. The introduction of inherently safer chemical processes is essential both to ensure the health and safety of all involved and to protect the environment.

In addition to health, safety and environmental driving forces pushing towards inherently safer chemical processes there are a number of other driving forces (or issues) which may come into play. These include costs, public concerns and customer pressure which can have a significant bearing on process and product development. Increasingly these are being taken into consideration.

1. INTRODUCTION

Inherently Safer Chemical Processes involve the use of smaller quantities of hazardous materials, the use of less hazardous materials, the use of alternative reaction routes or process conditions in order to reduce the risk of runaway exothermic reactions, fires, explosions and/or the generation or release of toxic materials. Such events in the past have led to multiple fatalities, severe damage to property, environmental damage and business loss.

It should be noted that in some cases changes made to improve the environment have resulted in inherently less safe designs. For example, the collection of vent discharge gases for incineration or for absorption on to carbon beds has resulted in explosions when the composition of the gases in the vent system has entered the flammable range.

The natural corollary to the design and use of inherently safer chemical processes is the design and manufacture of safer products. Such products would be beneficial to users as the risk to their health and safety could be reduced. Alternatively, or in addition, there may be an appropriate reduction in the potential adverse environmental impact by using these more benign or "greener" products.

2. METHODS OF INHERENTLY SAFER DESIGN

2.1 Intensification

The most widely used method of inherently safer design is intensification. This involves the use of minimal amounts of hazardous materials so that a major emergency is not created even if all the plant contents are released. For example, hazardous reactants, such as phosgene, are often generated as

This Note was produced by a Working Party of the Environment, Health and Safety Committee [EHSC] of the Royal Society of Chemistry.

The Society is a registered Charity. Its Royal Charter obliges it to serve the public interest by acting in an independent advisory capacity. In order to meet this obligation the members of the EHSC are drawn from a wide range of backgrounds and serve on the committee as individual experts and not as representatives of their employer.

The EHSC welcomes comments on this Note. Please send your comments to: The Secretary
Environment, Health and Safety Committee
Royal Society of Chemistry
Burlington House
Piccadilly
London
W1J 0BA

Tel: +44 (0) 207 440 3337
Fax: +44 (0)207 734 1227
Email: ehsc@rsc.org

EHSC Notes are also available on the Society's web site at www.rsc.org

EHSC Notes are updated from time to time and details of the most up to date versions can be found on the Society's website www.rsc.org

Version 2: 19/072007

required in adjacent plant so that the actual amount in the pipeline is kept to an absolute minimum.

Intensified designs are also available for reactors, liquid-vapour contacting equipment, heat exchangers, mixers, scrubbers, dryers, heat pumps etc. “Inherently safer” designed equipment is smaller than conventional equipment, often cheaper, as well as being safer because less add-on protective equipment is needed. In addition, buildings housing such equipment and plant are smaller and cheaper to build and maintain than conventional designs.

2.2 Substitution

If intensification cannot be achieved an alternative is substitution, the use of safer materials. Non-flammable or less flammable, less toxic solvents, refrigerants or heat transfer materials should be used instead of flammable or toxic ones. For example, some ethylene oxide plants use hundreds of tonnes of boiling paraffin to cool reaction tubes and this presents a bigger hazard than the mixture of ethylene and oxygen in the tubes. Modern plants now use water for cooling instead of paraffin.

Care must be taken to avoid introducing new hazards and risks as a result of substitution. For example, in order to protect the environment and prevent damage to the ozone layer, chlorofluorocarbon refrigerants are being replaced by liquefied petroleum gas and ammonia. However, this change can cause additional fire, health and safety risks if not properly controlled.

2.3 Alternative Reaction Routes

In addition to using safer chemicals it is possible to reduce the risks associated with manufacture by making changes in the reaction routes. The most widely quoted alternative route is for the product made at Bhopal, the insecticide Carbaryl. The reaction pathway involved reacting methylamine and phosgene to generate methyl isocyanate which in turn was reacted with α-naphthol to form Carbaryl. It was the release of the intermediate methyl isocyanate which caused the disaster at Bhopal. The alternative reaction route is to use the same raw materials but in a different order. Phosgene and α-naphthol can be reacted together to give naphthyl chloroformate. No methyl isocyanate is produced in this alternative reaction route.

When considering alternative reaction routes it is important to consider, in turn, the reactants, the catalysts, the solvents, the intermediates and the compatibility of all materials used. For example, in a particular process acetone was used as a solvent. However, it was realised because of the heat of reaction that the uncontrolled addition of one of the reactants or the loss of cooling would have led to a vigorous boiling of the mixture and result in the possible over pressurisation of the reactor and loss of containment. The simple replacement of acetone with toluene, which has a higher boiling point, eliminated this hazard.

2.4 Modified storage arrangements

If the above alternatives to achieve inherently safer processes cannot be applied and large quantities of hazardous material are still needed then it should be handled in the least hazardous form or in minimum quantities. Consequently, large quantities of ammonia, chlorine and liquefied petroleum gas are now usually stored as refrigerated liquids, at low pressure below their boiling point rather than under pressure at atmospheric temperature. If a leak occurs in such circumstances the driving force is low and the evaporation rate is comparatively small.

The inventories of toxic or flammable materials which are not manufactured on site, can be reduced significantly from hundreds of tonnes to tens of tonnes if reliable and regular supplies can be delivered, perhaps on a daily basis or on a just-in-time basis. In these circumstances a release of such materials, although still involving a comparatively large quantity, reduces the potential to cause injury or damage. This approach does not necessarily involve the modifications of existing plant, though smaller storage tanks would prevent inadvertent increases in the inventories in the future.

2.5 Energy Limitation

Consideration should also be given to limiting the amount of energy available in the manufacturing process. For example, it is better to prevent overheating by limiting the temperature of the heat exchange fluid than to rely on interlocks which may fail or be disconnected.

2.6 Simplicity

The final method of achieving inherently safer processes is to consider simplicity. Simple plants are inherently safer as there is less equipment to fail and fewer opportunities for human error.

3. SAFER PRODUCTS

The development of safer products arises from a deliberate decision to avoid risks to employees, users and, in some cases, to the environment completely by no longer undertaking the operation which gives rise to the risk. Examples include the substituting of asbestos by less hazardous alternatives in the manufacture of both insulation material and friction linings used in the braking and clutch systems of motor vehicles.

There are many examples of hazardous chemicals, such as benzene and other known carcinogens, which have been replaced by other chemicals that either have a reduced risk potential or have no known risks associated with them. The replacement of solvent-based paints and inks by water-based materials in the engineering and printing industries has not only reduced health risks, but has eliminated fire risks and led to environmental benefits by reducing the potential for pollution.

4. THE DEVELOPMENT OF INHERENTLY SAFER PROCESSES

In order to develop inherently safer processes along the lines illustrated above, several formal review procedures are available which can be applied to a new chemical process or during the review of an existing process. These procedures include Hazard and Operability (HAZOP) Studies, Life Cycle Assessment (LCA) Studies and the Guideword Led Hazard Identification Method. This latter procedure was proposed in a HSE funded project ‘Study on Inherently Safer Chemical Processes, and can be used as a stand alone technique, as a precursor to or as part of either a HAZOP or LCA Study.

HAZOP studies are normally carried out late in the design when detailed diagrams are available and it is then too late to make significant changes. However, similar detailed studies should be made a the very beginning of a project when decisions are made about which product to make, by what route and at which site.

The Guideword Led Hazard Identification Method requires a team approach involving a small group of development chemists, engineers and production staff, usually limited to six persons, including a chairman and a secretary. A flow diagram is given at Appendix 1 identifying the stages where inherently safety issues could be addressed within the process life cycle, starting with conceptual research and development through to plant decommissioning and environmental fate. It is at the conceptual stage in the process development where inherent chemical and process safety benefits can best be introduced. It becomes progressively more difficult to achieve such benefits in the later stages of process development.

The Guideword Led Hazard Identification Method is used to assess the proposed chemical process, one unit operation at a time. If a fire, explosion or toxic hazard exists in the unit operation then guidewords or hazard prompts can be used in pairs to stimulate discussion. The hazard prompts need to be selected prior to the workshop study. Typical hazard prompts that can be used in the development stage are given below.

Each prompt in the first list is considered in turn with each prompt in the second list:

Eliminate	Inventory
Minimise	Pressure
Substitute	Temperature
Moderate	Energy release
Simplify	Process equipment
	Unwanted reaction

e.g. eliminate energy release, moderate temperature or pressure, substitute unwanted reaction, etc..

In practice, some combinations may not be meaningful or may not raise concerns.

For appropriate combinations however the workshop study will discuss and record the following:

- the actual safety concerns raised;
- the possible consequences, i.e. the sequence of the events of concern;
- the safeguards or controls which should be provided to mitigate such consequences; and
- the actions arising including the provision of additional data for consideration or suggestions that other process options should be investigated.

The Guideword Led Hazard Identification Method must take full account of both legal and company requirements and should always be conducted by suitably qualified and experienced personnel.

5. DISCUSSION

In the past certain constraints have acted as brakes on the use of inherently safer chemical operations. These include the lack of time for process development, the fear of unforeseen problems, the influence of licensors and contractors who may have vested interests in large or expensive projects and the inability of the innovator to sell his or her ideas.

There have been, and will continue to be, problems associated with radical changes in process design required to achieve inherently safer chemical operations. Chemists and chemical engineers are understandably conservative in their outlook when tried, tested and profitable systems are likely to be replaced by a system which may be, at best, only partly proven. It is important, therefore, that chemists and chemical engineers are fully conversant with the principles of inherent safety and the benefits that can accrue from its application.

It must be remembered that a system or material change which is beneficial and cost effective in one area may not be the best solution elsewhere because of the local variation in cost or availability of critical resources. For example, the use of water-based paints to reduce hydrocarbon emissions and fire risk, places additional environmental burdens on organisations in the form of extra cost for effluent clean-up and/or disposal. In areas where water is a high cost resource, the installation of electrostatic painting, while perhaps expensive in the short term, may be a long term solution to the objective of safer operations. This process, however, can provide an early return on outlay due to collection and reuse of unused paint powder, thereby reducing running costs.

Inherently safe design, like all innovation, takes longer than copying the last design with a few added minor improvements. Inherently safe chemical operations will not be fully achieved unless or until designers are convinced that they are possible and desirable and that senior management are convinced of this necessity. Many designers have heard of inherently safe design but do not realise its full potential and senior managers still think that it is another safety gimmick. It is important that the message that inherently safe designs are possible and desirable continues to be spread through publications, conferences, meetings, etc. Organisations and individuals need to take a pro-active stance on the promotion of inherently safer chemical processes.

It must be borne in mind that there are commercial pressures to complete designs and get into production as soon as possible. As plants are being designed, ideas are often generated about various ways in which the design could be improved if more time had been available. These ideas should not be lost. They should be recorded so that they can be taken into account before sanctioning the next plant after the one that is currently being designed.

Whatever the circumstances, the fundamental changes necessary for inherently safer process design and development and the possible effect on the transportation, storage, waste disposal etc., need to be agreed and tested before being fully implemented.

6. CONCLUSIONS

The development of inherently safer chemical processes and safer products is not necessarily easy, demanding innovative thinking and fundamental changes to traditional modes of operation. Inherent safety is achievable through safer processes, improved engineering and stringent safety procedures. Inherent safety will be cost-effective in the medium and long terms, even if higher costs may be incurred in the short term. It should be pursued in order to safeguard the health and safety of all involved, including consumers, and to protect the environment. Inherent safety should become second nature to all those involved in the development of chemical processes and new chemical products.

6. FURTHER READING

- Chemical Industries Association, "A Guide to Hazard and Operability Studies", 1993.
- Health and Safety Executive HS(G)110, "Seven Steps to Successful Substitution of Hazardous Substances", 1994.
- Institution of Chemical Engineers Symposium Series No 141, "Process Safety – the Future", 1997.
- Institution of Chemical Engineers, Training Package, "Inherently Safer Process Design", 2005.
- R.E Bollinger et al, "Inherently Safer Chemical Processes – A Life Cycle Approach", American Institute of Chemical Engineers, 1996.
- Royal Society of Chemistry, "EHSC Note on Hazard and Operability Studies", 2007.
- Royal Society of Chemistry, "EHSC Note on Life Cycle Assessment", 2005.
- Royal Society of Chemistry, "EHSC Note on Risk Assessment at Work ", 2007.
- Royal Society of Chemistry, "EHSC Note on Safety Issues in the Scale Up of Chemical Reactions", 2007.
- T.A. Kletz, "Inherently Safer Design – Its Scope and Future", Process Safety and Environmental Protection, 81(6B):401-405, November 2003.
- T.A Kletz, "Process Plants – A Handbook for Inherently Safer Design", 2nd Edition, Taylor & Francis, Philadelphia, 1998.
- T.A Kletz, "Safer by Design", Chemistry in Britain, January 1999.

This Note was prepared by a Working Party of the RSC Environment, Health and Safety Committee [EHSC]. The members of the Working Party were:

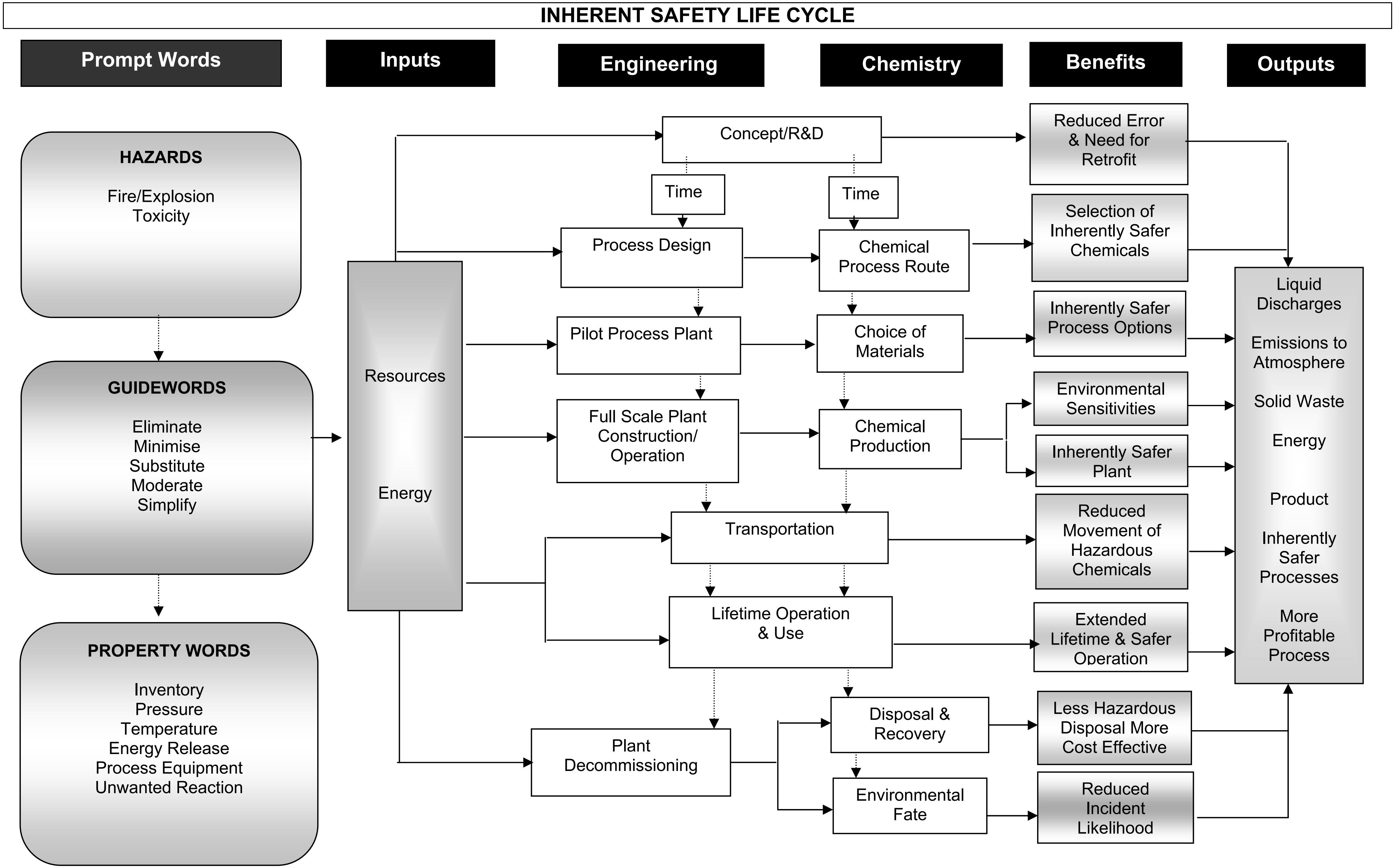
Dr I Wrightson [Chairman], Sara J Cooper, Dr M Crookes, Dr C L Grundy, Dr N King, Dr P Lewis,

Dr D H Lohmann, Dr C Maxwell, Dr G V McHattie, D Perry, Mr D M Sanderson and

Dr S Lipworth [Secretary].

The Working Party gratefully acknowledges the assistance of the Professor Trevor Kletz in the preparation of this Note, though of course the views expressed remain the responsibility of the RSC.

APPENDIX 1


INHERENT SAFETY LIFE CYCLE
Prompt Words
Inputs
Engineering
Chemistry
Benefits
Outputs
HAZARDS
Fire/Explosion
Toxicity
GUIDEWORDS
Eliminate
Minimise
Substitute
Moderate
Simplify
PROPERTY WORDS
Inventory
Pressure
Temperature
Energy Release
Process Equipment
Unwanted Reaction
Resources
Energy
Concept/R&D
Time
Time
Process Design
Chemical Process Route
Pilot Process Plant
Choice of Materials
Full Scale Plant Construction/ Operation
Chemical Production
Transportation
Lifetime Operation & Use
Plant Decommissioning
Disposal & Recovery
Environmental Fate
Reduced Error & Need for Retrofit
Selection of Inherently Safer Chemicals
Inherently Safer Process Options
Environmental Sensitivities
Inherently Safer Plant
Reduced Movement of Hazardous Chemicals
Extended Lifetime & Safer Operation
Less Hazardous Disposal More Cost Effective
Reduced Incident Likelihood
Liquid Discharges
Emissions to Atmosphere
Solid Waste
Energy
Product
Inherently Safer Processes
More Profitable Process