THE PROTECTION OF REACTORS CONTAINING EXOTHERMIC REACTIONS:

AN HSE VIEW

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SYNOPSIS

A number of exothermic reaction runaways occur in batch reactors in the UK every year.

The paper indicates the main causes of the incidents, and a strategy for reaction hazard assessment is outlined. Bases of safety, including inherently safe design and preventative and protective measures, are detailed.

Relevant legislation, guidance and HSE directed research is also discussed.

Keywords: EXOTHERM, REACTION, RUNAWAY, BATCH

1. <u>Introduction</u>

A number of incidents involving exothermic reactions in batch reactor systems are reported to the HSE every year. These occur when the reaction mass overheats in an uncontrolled manner leading to over-pressurisation and loss of containment.

This paper summarizes the main causes of the reported incidents. Chemical reaction hazards and the methods of prevention and control are discussed. Also, the principal legislation involved, the availability of guidance, and HSE sponsored research in this field are outlined.

2. <u>Main Causes</u>

A study by Barton and Nolan[1] examined 169 exothermic runaway incidents reported to HSE. The main causes were found to be:

- mischarging of reactants or catalysts
- little or no study of the reaction chemistry and thermo-chemistry.
- inadequate temperature control.
- inadequate maintenance.
- inadequate agitation.
- raw material quality.
- human factors.

The same underlying factors continue to be responsible for exothermic runaway incidents. These are:-

- a poor understanding of the reaction chemistry leading to badly-designed plant.
- under-rated control and safety back-up systems.
- inadequate procedures and training.

3. Reaction Hazard Assessment

During the development or modification of a batch reaction process, work will probably be conducted on a number of scales. In order to ensure safe operation, it is important that a reaction hazard assessment is carried out at each stage; ie during laboratory studies, and before transfer to pilot plant and full-scale manufacture.

A typical assessment procedure will involve:-

- defining the process, operating conditions and plant;
- evaluating the reaction hazards, including the effects of maloperation;
- selecting and specifying the safety measures;
- implementing and maintaining the safety measures.

The assessment should be structured and systematic so that all potential hazards and their causes are investigated. All foreseeable failure modes, including operator error, should be considered. Where appropriate, formalised methods should be used for hazard identification and assessing risk; eg HAZOP, fault-tree analysis, and HAZAN.

Assessments should be made by technically competent personnel with experience of chemical reaction hazards. Ideally the assessment team should operate independently so as to avoid conflicts between safety and production.

Reaction hazards can arise from:

- thermally initiated decomposition;
- self-accelerating exothermic reaction;
- rapid gas evolution, which may accompany thermo-neutral, endothermic and exothermic reactions;

Information required in order to determine the presence of reaction hazards includes:

- the thermal decomposition characteristics of the raw materials, products and by-products;
- the normal rates and total quantities of heat and gas evolved during reaction;

- whether exothermic runaway can occur;

Sources of information for the preliminary evaluation of reaction hazards include:

- thermochemical calculations;
- literature surveys;
- small-scale screening tests, eg Differential Thermal Analysis,Carius tube;

Care should be exercised when interpreting thermochemical calculations as the results may be misleading, particularly where unexpected changes of state, solution effects or side reactions occur. Literature surveys and calculations should be seen as good starting points but, in most instances some degree of experimentation will be required prior to large-scale manufacture.

Small-scale screening tests provide useful preliminary information, such as the possibility of thermal decomposition, exothermic runaway or gas evolution and the quantity and rate of heat generated. They enable a wide range of operating conditions to be investigated relatively quickly. Their main disadvantage, however, is that the test conditions tend to be isothermal while the conditions in a reactor runaway are nearer adiabatic. Therefore, the results need to be interpreted carefully as they may not be directly applicable to the large scale. For example, one common error is the assumption that the onset temperature on the full-scale plant will be the same as that determined in a screening test. Also, there can be problems with ensuring that the small samples used in the tests are representative of the bulk material.

Where the reaction hazards are significant and accurate data is required, more sophisticated test methods should be used, such as:

- adiabatic calorimetry, for examining the runaway potential of reactions and individual materials;
- specific measurements, eg test data for vent sizing;
- isothermal calorimetry, for determining reaction kinetics, heats of reaction, etc.

Where isothermal calorimetry is used to determine the kinetics of a runaway,it should be ensured that the reaction studied is the same as the one that occurs under runaway conditions.

The extent of the testing regime should reflect the complexity of the reaction system and the magnitude of the hazards identified. Further guidance on the testing for chemical reaction hazards has been published recently by IChemE[2].

4. Prevention and Control

The basis of safety for a chemical reaction process can only be selected once all the significant hazards have been identified and evaluated.

Where reasonably practicable, the hazards should be eliminated or their effects reduced by inherently safe design methods, for example:

- avoiding hazardous raw materials or intermediates (substitution);

- minimising hazardous inventories (intensification);

- designing the plant to contain the maximum pressure (attenuation).

The successful incorporation of inherently safe design measures depends on the reaction hazard assessment procedure starting at an early stage in the project development. For example, a change from all in batch to semi-batch processing, where the addition of reactants can be stopped if necessary, requires a different design concept.

However, in order to maintain a viable process significant hazards may still remain, and further safety measures will be necessary. These can be grouped broadly as "preventative" or "protective" measures.

Preventative measures include the use of sensors, trips, alarms, control systems, and other safety features which either take automatic remedial action or allow for manual intervention to prevent the conditions for uncontrolled reaction being achieved. These measures require a thorough understanding of the safe operating envelope within which the process must be maintained.

Protective measures mitigate the consequences of a runaway reaction. They are rarely used on their own, as some preventative measures are usually present to reduce the demand on the protective system. The main options are:

- emergency relief vents;

- crash cooling;

- reaction inhibition;

- secondary containment (eg blast protection).

A detailed knowledge of the runaway reaction is required for the specification or design of protective systems. For example, vent design requires knowledge of the rate of pressure or temperature generation under venting conditions.

Selection of safety measures for a particular application will depend upon a number of factors, including:

- the ease with which runaway can be prevented;

- the worst case consequences that could result;

- the applicability of the various protective measures;

- the compatibility of safety measures with the plant operation.

A common approach adopted by industry has been the provision of preventative measures, including control systems and safety trips, backed up by an emergency relief vent. The addition of a vent is seen as having a number of advantages:

- it has different failure modes to the preventative measures;
- it provides a relatively passive means of protection;
- it may still provide adequate protection if all other systems fail.

However, there are instances when companies decide not to incorporate an explosion relief vent. The main reasons given are:

1. Cost: In particular, plant required downstream of vents, such as knock-out pots, scrubbers or flares etc, may be prohibitively expensive;

2. Environmental: Where vented materials are too hazardous to vent directly to atmosphere and there are difficulties in designing effective or reliable downstream treatment/containment systems;

3. Technical: The required venting rates may be so high that it may not be possible to provide a large enough vent.

Where venting is not used, it may be acceptable to rely on preventative systems alone or to combine them with alternative protection systems. However, care should be taken to ensure the reliability of such combinations.

In addition, the safety measures should be supported by effective organisational procedures such as rigorous training, instruction and supervision of operators, maintenance and emergency procedures.

Whatever the basis of safety selected it is important that all foreseeable hazards are addressed and that sufficient safety systems are in place to reduce the overall risk to a level which is as low as reasonably practicable, in accordance with the legislation.

5. Legislation

The principal legislation in the UK controlling health and safety in the workplace is the Health and Safety at Work etc Act 1974[3] (HSWA). This places general duties on employers to ensure, so far as is reasonably practicable, the health, safety and welfare at work of their employees as well as the health and safety of other people affected by their undertakings. This duty includes providing a safe workplace, safe plant and safe systems of work along with adequate information, instruction, training and supervision. Employees also have a duty to take reasonable care of their own safety and that of others.

The Management of Health and Safety at Work Regulations 1992[4] implement the EC Framework Directive and apply to most work activities in Great Britain. These regulations extend the employers' general safety obligations under HSWA. In particular they require employers to assess the risks to employees and others from their undertakings and to put in place appropriate preventative and protective measures.

At most sites where there is a potential for a major accident, the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984, and subsequent amendments apply[5]. The Regulations require the manufacturer to identify all major accident hazards, to demonstrate safe operation and to report major accidents. At certain specified sites more stringent requirements apply, including the preparation of written safety reports and emergency plans.

Where the over-pressurisation of chemical plant is reasonably foreseeable, eg. in exothermic batch reactors, the Pressure Systems and Transportable Gas Containers Regulations 1989[6] apply. The Regulations include a requirement to provide and maintain protective devices to prevent danger.

The Provision and Use of Work Equipment Regulations 1992[7] cover the provision of safe work equipment and its safe use. The term "work equipment" includes chemical reactor systems. The regulations include the requirement to prevent exposure of persons to specified hazards, including the unintended or premature explosion of the work equipment.

The Control of Substances Hazardous to Health (COSHH) Regulations 1988[8] require the assessment and control of toxic substances in the workplace. All sources of exposure are covered, including accidental releases resulting from explosion or venting.

6. <u>Guidance and Research</u>

The review by Barton and Nolan[1] highlighted the need for guidance in the following areas:

- chemical reaction hazard assessment;

- vent sizing;

- safety-related control systems;

The topic of disposal/containment systems for vented material was added following recent concern about protection of the environment.

In the area of chemical reaction hazards, HSE has sponsored a number of research projects at South Bank University (SBU). These were aimed at appraising existing laboratory techniques for assessing chemical reaction hazards. The SBU work is summarised in reference 9, and has contributed significantly to the development of guidance on this topic. The book "Chemical Reaction Hazards", a collaborative venture by HSE, Industry, SBU and IChemE, has just been published by IChemE[2]. It provides a basis for good practice in assessing chemical reaction hazards. Additionally, HSE have produced a training video on the topic, entitled "The Control of Exothermic Reactions" which is also available from IChemE.

With regards to vent design, HSE was a member of the Design Institute for Emergency Relief Systems (DIERS). DIERS was a consortium of 29 companies formed under the auspices of AIChE, to develop methods for the design of emergency relief systems for runaway reactions. This work represents the current state of the art and is based on both theory and experiment. A project manual has recently been published by AIChE[10].

As the DIERS methodology was never fully validated, research is being carried out at HSE's Buxton research laboratory to examine the applicability of the DIERS work to the large scale. A 250 litre pilot-plant facility has been constructed and trials are in progress[11].

HSE is also sponsoring research at Sheffield University aimed at refining the equations for vent sizing of "gassy" systems.

Preliminary advice on the design of disposal/containment systems is available in a recently published HSE Contract Report[12] but it is not HSE guidance.

Regarding safety-related control systems, cross-industry guidelines on the selection of safety systems have been proposed by the International Electrotechnical Commission (IEC) in draft standard IEC/TC 65A[13]. The document introduces the concept of the "Safety Lifecycle" which sets out procedures for the safe design, operation, and modification of processes, from conception through to de-commissioning.

Conclusions

1. Exothermic runaway incidents, resulting from a poor understanding of reaction chemistry, under-rated control and safety back-up systems and inadequate procedures and training, continue to be a cause for concern.

2. To ensure safe operation, a thorough reaction hazard assessment should be carried out prior to each stage of process development or modification. The depth of the assessment should reflect the complexity of the reaction system and the magnitude of the hazards identified.

3. Where reasonably practicable, the reaction hazards should be eliminated or reduced by inherently safe design methods. Significant residual hazards should be reduced by preventative and/or protective measures.

4. The basis of safety should be such that there are sufficient safety systems to reduce the residual risk to a level which is as low as is reasonably practicable.

5. IChemE have recently published a guide to chemical reaction hazards. HSE are directing research to further guidance on preventative and protective safety measures.

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