Hazardous substance release following inadequate HAZOP studies

21 September 2010

Heilbronn

Germany

Hazardous releases
Risk assessment
Human factor
Design

THE FACILITIES INVOLVED

The facility :

The company is a manufacturer of additives for the paper and leather industry. It is located in the industrial area of the town, with a number of other companies in close proximity. The site has been occupied by the company since 1947 with modifications and extensions over the years. The chemical operations are carried out in multi-purpose batch reactors.

The unit involved :

RR

Fig. 1: A view of the reactor after the incident

The unit involved in the accident was a multi-purpose batch reactor fitted with glass reflux condensers, a bursting disc of nominal bursting pressure of 0.8 bar overpressure. Operation of the reactor is a mix of manual and process controlled operations.

The reactor was connected to a water tank of capacity 32 l by a pipe. In the pipe there were two valves. The valve at the lower level was manually operated, the valve at the higher level was normally open and designed to be shut automatically on activation of the overpressure alarm at 0.5 bar. The manually operated valve was supposed to be closed before starting the hydrolysis reaction.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident :

A failure in the addition of water to a reactor (30 litre added at once instead of in 3 litre aliquots) led to an exothermic runaway reaction. The foaming contents of the reactor broke the glass condenser and led to the release of HCl vapour (ca. 60 kg) to the atmosphere.

Against the intended operation, the manually operated valve was open, which meant that when the process was started and the process controlled valve opened the entire contents of the 30 l tank ran straight into the reactor. Although the overpressure alarm (0.5 bar) was triggered, this was too late to prevent any flow into the reactor.

The release of the HCl cloud inside the reactor building triggered the fire alarms and notified the fire brigade. An employee switched the building ventilation on which led to the spreading of the HCL vapour outside of the building and affecting the surrounding area.

Consequences of the accident :

Seven people outside of the establishment required medical attention, two of them were kept overnight in hospital. Damage to the equipment was limited to the broken glass condensers and large scale contamination of equipment and the outside of the reactor with the reactor contents.

The European scale of industrial accidents :

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the '*SEVESO II*' Directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices :

The parameters composing these indices and their corresponding rating protocol are available from the following Website : http://www.aria.developpement-durable.gouv.fr

The "Hazardous Materials Released" index was not rated given the nature of the substance released (HCl does not belong to the Seveso list).

The "Human and Social Consequences" index was rated a "3" due to the injuries sustained by 7 people outside the establishment, including 2 overnight hospitalisation.

The "Environmental Consequences" index was not rated given the absence of any impacts on the environment.

The "Economic Consequences" index was not rated given the economic damages lower than 100 k€ (30 k€).

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The reaction was the hydrolysis step in a multi step process carried out in the same reactor.

The first step was the reaction of an organic phosphate ester chloride with a fatty alcohol. In the following step water is added, liberating HCl (see below) - this is the step which failed. Finally, the hydroxyl groups were to be reacted with NaOH, liberating water.

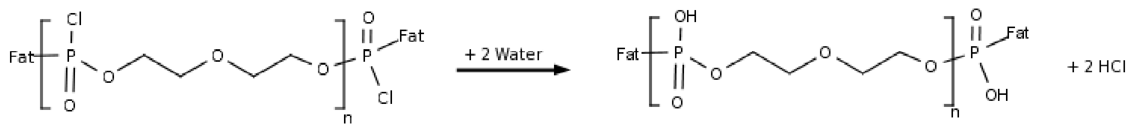

Fig. 2 : The hydrolysis step, which liberates HCl, and was the process step which failed

Within the company's Safety Management System the reactions had been assessed using the HAZOP (Hazard and Operability) method to identify the hazards and the potential consequences of deviations from the intended operation.

The HAZOP had identified the hazard potential of adding too much water as loss of control of the reaction, but only indicated that the standard operating procedures (SOP) should be improved. Standard operating procedures are not suitable for controlling the potential loss of control of a reaction. In this case only an inherently safe design through which the addition of maximum 3 litre aliquots to the reactor at one time was possible could have prevented the accident under manual control.

Other methods for handling "runaway-reactions" which are dependent on process control systems would only be able to react once the water had been added and the pressure had risen to a critical level. Pressure relief systems for foaming contents require detailed knowledge to be able to design them.The best approach is to ensure that the reaction "runaway" cannot occur in the first place.

An inspection of the plant revealed that the design of the apparatus did not deal with the human factor aspects of operating the reactor adequately.The 30 litre water tank was connected by a pipe to the reactor, the flow in the pipe was controlled by two valves, one of which was manual and should have been closed at the start of the operation, the other being electronically controlled by the process.The second valve was normally open and it was intended that it should close in the event of an overpressure.The manually operated valve was without position markings, and the physical position of the valve was difficult to see. When the accident occurred the manual valve was open; starting the process step to add water opened the electronically operated valve and all 30 litres of water were added at once. The control systems could not respond to prevent any build up of pressure.The peak pressure of the foaming contents was sufficient to break the glass condenser, but was below the nominal pressure of the bursting disk, which was undamaged.

The conception of the automatic control system was fundamentally flawed, as it could only respond once the high pressure alarm had been triggered. In this case all of the water was in the reactor and shutting the valve had no effect.

ACTIONS TAKEN

The plant has since been modified to limit the maximum volume of water which can be added at one time and to improve the electronic control system.The HAZOP studies have been reviewed for all exothermic reactions carried out on in this apparatus. In particular attention being paid to consequences of operating failures and a balance between risk control measures and the potential severity of the consequences.

LESSONS LEARNT

Two main lessons can be learned from this accident :

1. The hazard identification within a HAZOP study must be coupled with a balanced and appropriate approach to risk mitigation and control. Hazards which potentially may lead to loss of control of the reaction require either an inherently safer design approach or highly reliable, fast acting electronic process control systems.

2. The design of the reactor and its peripheral equipment should take account of human factor aspects and support the workers in the operation. This means it should be clearly visible which valves are open or closed. Interlocks and control systems should be used to prevent failures which can lead to the loss of control of the process.