(Article Published in The Chemical Engineer – Oct 2001)

EMERGENCY RELIEF AND CONTAINMENT SYSTEM FOR A HIGHLY HAZARDOUS PROCESS

By Keith Middle - Senior Process Safety Specialist
Chilworth Technology Ltd, Beta House, Chilworth Science Park, Southampton, SO16 7NS, UK

In today's operating climate, the provision of safety solutions can often bring us into conflict with other requirements. For example, protection of reaction vessels against overpressure used to be a simple case of relieving the pressure to atmosphere via a relief valve or bursting disc assembly. However, nowadays there is, justifiably, a lot more focus on the environmental impact of relieving to atmosphere. Add to this the fact that the hazardous nature of some materials can include pyrophoric behaviour and a tendency to decompose violently under certain circumstances, and it can be seen that the provision of safety solutions can include a combination of different technologies and innovative thinking. This was the brief given to Chilworth Technology when FMC decided to upgrade its organolithium production facilities at its Merseyside site, improving the reaction and safety control system and focusing on the emergency relief and disposal facilities for each of its processing vessels. The quench tank solution devised and specified by Chilworth Technology with detailed engineering by Jacobs Engineering lead to a successful project, culminating in the team winning the 2001 Severn Trent Water Safety Award at the IChemE Safety and Environmental Awards ceremony.

Characteristics of the Process

The organolithum production process involves producing an activated form of lithium metal, and reacting this with an organochloride in a semi-batch procedure. The highly exothermic reaction has rapid kinetics at the normal reaction temperature and is hence feedrate controlled, although the reaction may stall at lower temperatures leading to reactant accumulation. The extreme density differences of the various components can lead to layering in the case of agitation failure. On completion of the desired reaction, the highly reactive, pyrophoric liquid product is separated, purified and conditioned.

Hazard assessment studies identified two major categories of risk to the low pressure production vessels, runaway chemical reaction owing to potential reactant accumulation and fire engulfment leading to material decomposition. Chemical reaction hazards testing determined that the heat of reaction was such as to predict a potential adiabatic temperature rise of ca. 1000 K (i.e. fully vaporised) in the event of an "all-in" batch, whilst the onset temperature for decomposition (resulting in considerable gas generation) of a typical product can occur at temperatures close to the operating conditions. Even limiting the potential accumulation to 20% and setting the bursting disc to a rupture pressure where the decomposition onset would not be reached, yielded an impractical vent diameter of ca. 75 cm.

Safety Strategy Adopted

It soon became clear that no emergency relief system could be expected to cope with substantial levels of reactant accumulation. Semi-batch processing is an inherently safe operating approach, provided that equipment or control failures cannot turn it towards a batch process. The design of a high integrity protection system to back-up the DCS process control system, was consequently selected as the basis of safety for the control of runaway reaction hazards. Such a system needed careful analysis, the detailed design being verified to IEC61508 Safety Integrity Level 3. This then took the most severe process deviation out of the design basis for the emergency relief system.

Nevertheless, even the finest safety control system cannot protect against external threats, foremost of which is often fire. In a building handling pyrophoric materials, designed to exclude water (the product is highly reactive with water evolving hydrogen), fire is an ever-present risk. The vessel relief systems therefore have to be designed to handle this case, with the foamy fluids being shown during laboratory testing to vent 3-phase. Additionally, owing to vessel restrictions low venting pressures are necessary, whilst being an infrequent event, passive treatment measures are preferred.

Previous Emergency Relief and Disposal Approach

The existing plant had a relief system where the vents discharged into a ground level burning pit, sited local to the plant building.

Figure 1 Ground level burning pit.

The idea was that the pyrophoric materials were allowed to burn in a semi-controlled fashion in the event of disc rupture. The principal concerns with this approach were:

- Although pyrophoric, any failure to self-ignite would lead to a low level flammable cloud, adjacent to the plant, which could subsequently cause an uncontrolled vapour cloud explosion
- Suck-back of air into the vessels once the overpressure was controlled, with subsequent potential for semi-contained explosion
- Environmental discharges due to uncontrolled combustion
- A highly visible event at the boundary of the site, which abuts a Site of Special Scientific Interest

A sister site of FMC at Bessemer City, US had a similar design for their disposal system and was equally dissatisfied. Their proposed solution was the installation of a flare stack to handle the relief discharges. Their design was dropped in favour of the Merseyside solution once its merits were appreciated.

Design Aspects of the Emergency Relief Network and Quench Tank

The solution to the relief system disposal proposed by Chilworth Technology was a quench tank. This would offer a passive system designed to recover the liquid and solid phase materials in the relief stream, condense the vapour components to minimise flammable releases, dissolve any gases from material decomposition, and act as a seal against air ingress into the vent network at the completion of venting. If correctly designed, the quench tank outlet stack would release practically nothing to atmosphere.

In order to limit the scope of the project, it was decided that the quench tank be designed to serve only the 25 vessels handling pyrophoric materials; a separate system would be installed to handle the solely flammable fluids. The primary design basis would be for the relief streams under fire conditions, although spurious disc failure and physical overpressure events would also be considered. A close review of the vessel layout and production scheduling was conducted to determine the number of vessels likely to be involved in an incident. This analysis included an assessment of the extent of any fire, bearing in mind the single building two floor layout, the vessel solvent inventories, the pumping rates of feed headers, the solvent burning rates and the building drainage features. It was concluded that simultaneous peak venting from more than one vessel was unlikely, but that consecutive discharges from adjacent vessels could occur. The design for the tank would consequently be based upon the release from 5 large vessels.

Individual vent lines from each vessel were connected into a header network. The vent network design grouped the plant vessels into 4 headers, based upon the vessel sizes, the venting probability and the geographical layout. DIERS vent sizing calculations for 2-phase flow were used to establish the appropriate line sizes, whilst the pressure profiles through the network were adjusted to provide a driving force for dispersion in the quench tank. Twin bursting discs were used in each vent line to prevent this varying network back-pressure from influencing the rupture disc opening pressure. The resultant design lead to a system of typically DN150 vessel relief lines feeding into a DN300 header system. The mechanical design of the network involved close analysis in order that it was sufficiently robust to resist the considerable forces involved during 3-phase discharges, but nevertheless allowed thermal expansion during the incident and restorative maintenance after the event.

The design of the quench tank starts with the choice of quench fluid. An ideal solvent is one that is non-reactive to the relief stream, stable, non-volatile, non-foamy, non-toxic, has a high heat capacity, and does not freeze during winter. Often water makes an ideal quench fluid, but in this case it failed the first criterion being highly reactive with organolithium and pure lithium. Mineral oil was the chosen fluid.

A series of laboratory experiments were conducted to gather key data for the design including:

- the peak allowable temperature before product decomposition occurred
- the vapour / liquid equilibrium behaviour of the solvent / oil mixtures
- the foamy nature of the discharge flow
- the ability of the oil to condense the vapours
- the pyrophoricity of the product / oil mixtures

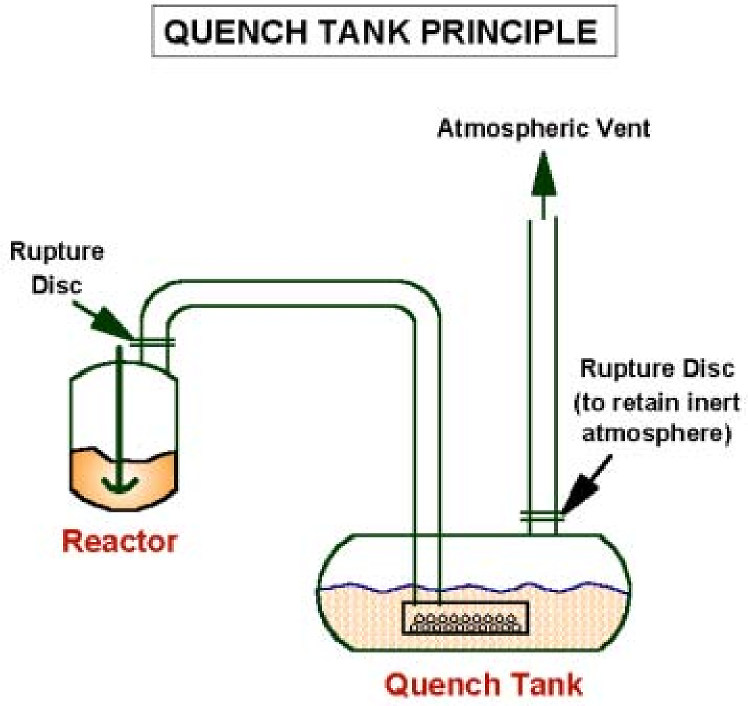

Figure 2 Quench tank principle.

This data allowed overall heat and mass balance calculations to be conducted for the quench fluid under different sets of conditions. The basic calculation resolves the quantity of oil required to condense and cool the incoming stream, whilst the whole mass is not allowed to heat-up beyond a determined peak temperature. The overall dimensions of the tank are then calculated for the quantity of fluids contained, assessments being made of the degree of fluid aeration, required freeboard for droplet disengagement and required liquid depth for effective vapour condensation. An additional constraint on the vessel dimensions is the fact that 4 separate inlet headers need to be accommodated beneath the liquid level. This lead to the choice of a horizontal tank.

The relief streams need to be dispersed as they enter the quench oil in order to promote mixing and prevent “water hammer”. A perforated pipe sparger was chosen, although other designs such as jet condensers could be used. Flexibility is required of the sparger since it has to handle an evolving fluid stream, from high pressure 3-phase material to low pressure gases and vapours, depending upon the venting conditions. Principally, of course, it must not block! The key to the sparger performance is hole size and number / layout. Holes too large will cause vibration, whilst too small and they will be more susceptible to blockage. Laboratory trials had demonstrated the flowability of the 3-phase materials along small diameter lines, so there was added confidence of the sparger design approach. Once the sparger process design was finalised, detailed mechanical design was required to develop a symmetrical arrangement to balance the forces, and equally withstand the surging that would inevitably arise during operation.

Figure 3 Quench tank installation showing inlet lines to sparges.

Owing to the nature of the fluids, the design of the vent network and the quench tank included inert gas purging facilities. These ensured that an inert atmosphere would be present when the system was called into operation, and that air would be excluded during cool down following an incident.

Close attention was paid in the overall design to the maintenance of the system, both under normal conditions and particularly following a venting incident. One criterion for the quantity of oil chosen for the quench fluid was that it would dilute the discharged material to below its pyrophoric concentration. To allow inspection and cleaning of the 4 spargers, a design was developed to allow their withdrawal without taking the tank off-line or exposing the spargers to atmospheric conditions. Spray cleaning facilities were also designed for the tank. Oil flush and deactivation facilities were provided for the vent network to allow its preparation in advance of dismantling. The final advantage of using mineral oil as a quench fluid relates to the fact that it is compatible with the normal production operation; thus the contents of the quench tank can be recycled to the plant processing equipment for on-site disposal and clean-up.

Figure 4 Quench tank site and installation.

Conclusions

Major improvements have been achieved in the provision of safety facilities for the manufacture of a highly hazardous organolithium material. Elimination of runaway reaction hazards has been achieved by a thorough understanding of the thermochemistry of the reaction and the installation of a high integrity protection system designed to IEC61508 SIL 3. Re-engineering of the emergency relief facilities for all vessels has provided protection against non-controllable hazards, such as external fire engulfment of the process vessels. Rather than compromising the environmental protection as is often the case when considering the discharge of emergency relief systems, the new quench tank installation provides substantial improvements over the former situation. Emissions are eliminated, workers are protected both during the incident and during recovery maintenance, and large visible plumes of flame and smoke do not alarm the neighbours.

For further information on products and services available from Chilworth Technology please contact the Marketing Department at:-
Chilworth Technology Ltd
Beta House, Chilworth Science Park, Southampton, SO16 7NS, UK
Tel: +44 (0)23 8076 0722 Fax: +44 (0)23 8076 7866
Web: www.chilworth.co.uk Email: info@chilworth.co.uk