

METHODOLOGY FOR SELECTING DISPOSAL SYSTEMS FOR CHEMICAL REACTOR RELIEF

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Environmental concerns are such that the previously established practice of venting chemical reactor relief systems directly to atmosphere, is no longer acceptable. This paper describes a detailed decision tree which allows determination of the most appropriate downstream treatment/disposal method. It provides supplementary information and references, to allow decisions to be made and appropriate methodologies to be chosen, at an early stage in the design process.

Reactor Relief Venting Disposal Design
Methodology

INTRODUCTION

The common practice for disposal of chemical reactor relief streams has been release direct to atmosphere. This arrangement has the advantage of being both cheap and reliable, however, increased safety, health and environment (SHE) considerations, are making this no longer acceptable and future legislation will, almost certainly, become stricter, even for infrequent plant emissions, such as emergency reliefs.

It is necessary when designing any treatment/disposal system to ensure that all the relevant SHE criteria are met. Commercial considerations, such as the value of a material (e.g. in pharmaceutical manufacture) may also have an impact on the design decisions.

Previous papers dealing with this area have been written by Burgoyne and Kneale (Ref. 1,2). This paper gives a systematic methodology, in the form of a logic diagram, which ensures that all relevant criteria are considered in selecting the most appropriate discharge and disposal system.

SELECTION OF DISCHARGE/DISPOSAL SYSTEM

The logic diagram (Figure 1) ensures that all SHE and other criteria are taken into account when arriving at a decision on the most appropriate discharge/disposal system for a chemical reactor relief stream.

Guidance is given for each decision box and is a summary of the considerations required before taking each decision. It is important that early consideration is given to the design of any discharge/disposal system, as the relief stream design is easier, when done as a whole. Later "add-on" solutions can be problematic and where possible, the decision should be made at the same time as relief design. The logic diagram should help in making

early decisions on discharge/disposal requirements. The guidance reflects this, by providing enough information to make preliminary decisions and referencing more detailed design data where required.

The logic diagram arrives at the final point of release of material to the environment (boxes 4, 7, 8, 17, 18, 19 and 20) and not simply pointing to an appropriate piece of plant equipment. This is an important consideration, as it is the final destination of relieved materials which is most affected by SHE criteria. Where there is no acceptable means of discharge/disposal, the necessity to reconsider the process is also included as an option.

Where separation is required the logic diagram treats gas/vapour and liquid/solid streams as separate entities. This ensures that each component has been subjected to the full set of criteria.

Boxes 10, 11, 12 and 13 cover the equipment for downstream treatment. The design of such equipment can be complicated, especially for emergency relief systems, where they have to operate reliably to deal with large, infrequent, peak loads.

All equipment must be designed to cope with the maximum possible flow through the relief vent line and not just the required relief rate. This is especially important where a relief stream will contain 2-phase flashing flow. This means that overdesign of relief streams, by the use of large safety factors will introduce large penalties in the design of any downstream treatment equipment. Some over-design may be necessary to accommodate future (economic driven) process changes, eg increased concentration, volume etc.

GUIDANCE FOR LOGIC DIAGRAM

Box 1: Valuable Material

Some relief streams contain products which have an intrinsic value (e.g pharmaceuticals, metal catalysts etc). Retreatment and/or reprocessing may be necessary following recovery.

Box 2: Hazardous Material

Consideration should be given to whether the relief stream is toxic, asphyxiant, malodorous, corrosive, flammable or environmentally damaging. The quantity of material released and the likely size and duration of any hazardous region has to be determined.

Toxicity: The toxicity of the materials in the relief stream has to be considered. An estimation of the size of the cloud formed following discharge needs to be made. The concentration and exposure time is then compared with the relevant hygiene standards to determine whether the release is acceptable. Toxic concentrations are usually far lower than flammable concentrations and the size of 'unacceptable' toxic clouds is larger than those for flammable atmospheres. Discharges which contain liquids or solids and those where the material can condense to form fumes or mist produce high local concentrations. Where discharge is due to decomposition, rather than runaway of the desired reaction, toxicity data may be difficult to obtain.

Asphyxiation: Some substances (eg nitrogen, carbon dioxide) although not poisonous when inhaled, can cause physiological effects which are hazardous to health, by oxygen starvation and may need special consideration.

Malodorous: Odour threshold levels are generally well below toxic concentrations. Although not hazardous, odours are often more of a nuisance problem. However, they do need to be considered and a decision taken as to the levels required to prevent adverse publicity.

Corrosive: Materials may be inherently corrosive or corrosive compounds may be formed by contact with the atmosphere during discharge. Corrosive substances may be damaging to personnel, plant equipment, public property or the environment. Neutralising agents may be needed but this can give rise to further hazards caused by chemical reaction.

Flammable: Combustible material can be in various forms, such as mists/sprays, gas, vapour, or solid. Flammability hazards arise when the concentration exceeds the lower explosive limit. Typically lower limit values for carbonaceous materials lie in the range 3-50 g.m⁻³. Specific values from the literature should be used for design purposes (Le Chateliers rule can be used to calculate the composite lower limit value of flammable gas or vapour mixtures).

Relief streams, particularly from runaway chemical reactions, will often be at elevated temperatures which widens the flammability limits. As an approximation, lower limit values are decreased 8% by a temperature increase of 100 deg C. Similarly, upper explosive limits are increased approximately 8% by a temperature increase of 100 deg C.

Note needs to be taken of the possible presence of oxidants in the discharge (e.g oxygen, chlorine, etc) which may enhance or change the flammability characteristics of the emission.

Where the discharge contains components which can give rise to the generation of flammable atmospheres, an assessment of the ignition risk is required. Consideration should be given to, electrostatic charge generation (mist, non-conducting polymeric materials/plant, insulating liquids, etc), auto-ignition, pyrophoric materials, lightning, etc.

Environmentally Damaging: Concentrations of toxics or pollutants which cause harm to plant and/or animal life can be extremely low (parts per billion). The effect of the discharge on the environment needs to be considered.

Box 3: Discharge Locally

Discharge local to the equipment may be inside a building, or within a work area. Additional hazards may arise from heat (e.g steam) or high pressure (resulting in excessive noise and/or poor visibility).

Box 4: Safe Local Discharge

Discharges of innocuous liquid or liquid/solid suspensions may be released close to a drain, but away from walkways, to an effluent treatment system provided that the discharge (taking account of quantity, rate and frequency) is acceptable. The possible presence of people needs to be assessed.

Box 5: Recover Valuable Components

Valuable components of relief streams can be recovered using techniques such as separation tanks, knock-out pots, scrubbing, condensation, dump or catch tanks. Where the system exhibits natural foaming tendencies the additional problem of phase separation needs to be considered.

The logic diagram assumes that the valuable component(s) is the condensed phase (i.e liquid and/or solid).

Box 6: Dilute to an Acceptable Concentration

Consideration has to be given to whether the discharge can be readily diluted to a concentration that is acceptable at the expected frequency.

Dispersion of gas/vapour is important with respect to the discharge of noxious or hazardous substances to atmosphere. Consideration should be given to "fall out" (solids or liquid droplets) which may occur close to the discharge point. The degree of dilution and dispersion will be governed by jet mixing, buoyancy effects and turbulence. "Slumping", where any cloud formed falls to the ground may occur with heavier than air discharges. Less dilution may occur towards the end of relief, through non-reclosable relieve devices, producing high local concentrations and possibly more "slumping". In certain cases, fine wire, rupture disc detectors can be used, to activate control valves (e.g on feed lines) to minimise the period of the release.

Enhanced jet mixing requires a discharge velocity $>$ mach 0.6.

For flammable materials dilution to less than 25% of the Lower Explosive Limit (LEL) is required to ensure the release is non-flammable.

For releases involving less than 2 tonne of hydrocarbon into the atmosphere but away from neighbouring structures, there is little if any risk of an unconfined vapour cloud explosion (i.e causing damaging pressure effects). Explosion hazards can result, however, from the release of much smaller quantities of material into confined or partially confined spaces. Releases of highly reactive materials (e.g hydrogen, ethylene, ethylene oxide etc) can cause damaging pressure effects even in small quantities (i.e 100 kg or less) and require special consideration.

Box 7: Discharge to Specified Area

Noise: A nuisance problem to neighbouring residents but potentially harmful to plant personnel. Noise levels can be approximated from simple formulae. This may also be a source of physiological "shock" to process operators. The noise from a gaseous release is proportional to the velocity to the power 6-8. Site boundary limits of 5 dB(A) above background should be aimed for.

Poor visibility: Proximity to public rights of way needs to be considered. Liaison with the local authorities (police and fire brigade) may be needed to establish contingency measures.

Fire: Ignition of unconfined flammable material resulting from external sources such as welding equipment, electrical apparatus, motor vehicles, etc, may give rise to fire/radiation hazards.

Estimates of the possible harmful effects of heat exposure may need to be assessed.

Where the velocity of a flammable atmosphere is $< \text{mach } 0.3$ a stable flame can be formed on the end of a vent line.

The recommendations for design of flarestacks in API RP 521 (Ref.3) can be used to ensure that the location and height of any possible flame is arranged such that the radiation does not exceed:

- 1.7 kW/m^{2*} where personnel may be continuously exposed.
- 4.7 kW/m^{2**} where people may be present but can quickly escape.
- 6.3 kW/m^{2**} where personnel are required to take emergency action in appropriate protective clothing.
- 38 kW/m^{2*} on adjacent vulnerable equipment (assuming that cooling water could be deployed quickly).

BOX 10: Phase Separation

The separation of gas/vapour phases from liquid/solid phases is desirable in most cases. This can be done by inertial techniques include gravity settling and cyclone/knock-out pots. There are some design complications since the particle size distributions may not be known and the rates of flow and flow velocities may vary greatly during the release. Condensation/scrubbing may also be required downstream for noxious gases/vapours. Secondary reactions (chemical) or explosion hazard in equipment downstream from the relief device also needs consideration (see BOX 2).

Phase separation of releases which are inherently foamy will require special consideration.

Special consideration will also be required for molten materials which solidify on cooling, the dump tank/catch pot may need to be heated. Vent pipes may also require trace heating. A single relief device (RV or BD) is unlikely to be acceptable due to the risk of leakage and blockage in the vent pipe.

Design should take account of:

- (a) The maximum quantity of material to be discharged (probably aerated) when delivered at the **maximum vent capacity**
- (b) Venting the non-condensed phase to atmosphere directly, or via a scrubbing/incineration system.
- (c) Requirements for explosion prevention or protection in downstream equipment such as, discharge under water, explosion suppression, explosion venting, inert gas blanketing.
- (d) Trace heating or anti-freezing additives to prevent blockages on cooling.
- (e) Heat balance to take account of temperature increase caused by condensation and liquid cooling.

- (f) Allowance for any vortexing, caused by impingement of the relief stream on the liquid in the separator.
- (g) Provision for emptying facilities.
- (h) Further chemical reaction, or decomposition, in tank.
- (i) Loss of an inert gas blanket, if present, in the reactor following relief.

(see also BOX 2 notes)

References (3-10) give the best practice design methods available.

BOX 11: Treat (eg Quench, Absorb)

Treatment of relieved material can involve dissolving, diluting, drowning, adsorbing, absorbing, reaction and condensing.

Quenching can be used in conjunction with a separation/knockout device/tank. The method can utilise chemical reagents to render the discharge innocuous and prevent further reaction. Alternatively, the reaction can be quenched physically (i.e drowned out) by providing a heat sink such as water. Heats of neutralisation need to be considered when estimating temperature rises (to prevent boiling).

References (9-13) give the best practice design methods available.

Secondary treatment of the non-condensed phase (gas/vapour) may often be required downstream from the separation vessels. The selection of a suitable scrubbing liquor depends on the process chemicals and vented gases. It is axiomatic that the liquors should not cause a further chemical reaction hazard. Scrubbing devices should be sized on the **maximum vent capacity** and generally run continuously. Absorption systems can therefore be very large and may only be effective on one gaseous product, ie multiple devices may be required. Account needs to be taken of the demand from normal process vents when using "common" scrubbers.

References (14-15) give the best practice design methods available.

BOX 12: Secondary Containment

A second vessel can be used to capture all of the vented material without relieving to atmosphere. This can be used in conjunction with quenching/cooling or merely by providing additional gas/vapour space. Flammability and explosion hazards also need to be considered, including the effect of increased pressure. The technique can be useful for foamy systems involving valuable material. The effect of increasing back pressure should be considered especially where safety valves are used. Back-to-back discs may be needed to prevent reverse pressure effects prior to disc rupture. The maximum allowable pressure in the containment vessel is equal to 50% of reactor disc bursting pressure (absolute). This is to ensure choked flow throughout relief. A second vessel (and services) may not be cost effective. Cleaning and down-time caused by solid residues from decomposition reactions are also important.

Reference (16) gives the best practice design methodology.

BOX 13: Flare

Flaring is both efficient and economic for large installations handling combustible gases and is most common in the petroleum and petrochemical industry, on and off shore. Thermal radiation hazards and noise can be a problem (see BOX 7). Unless existing on site, flaring may be uneconomic and impracticable.

Incineration in a furnace (e.g open fired boiler) is a method ideally suited to the controlled flow of relatively small quantities of material which will decompose/pyrolyse at furnace temperatures and is particularly useful for malodorous/offensive materials. An assessment of the flammability of feed composition is needed and the oxidant level needs to be reduced to an acceptable level to prevent back propagation of flame and any subsequent risk of detonation in long sections of pipework. Attention also needs to be paid to production of oxidants (e.g O₂, Cl₂, NO_x) from reaction and other source (risk of air ingress etc). Safety can be achieved by inerting the line (e.g with N₂).

The position of the vent inlet to the combustion chamber needs to be carefully designed and draughting at the inlet may be required to prevent an accumulation of flammable gas and the subsequent explosion risk. A separation device may also be needed to prevent flammable liquid from entering the furnace. Consideration should be given to condensation in the pipework.

A flame trap (to prevent back propagation) is not normally acceptable for the following reasons:

- (a) Cannot use near boiler/furnace - too hot
- (b) Prone to blockage
- (c) Positioning remote from furnace (in cooler pipework) may allow run-up to detonation between the furnace and the flame arrester. Detonation arresters are available but are large and can be prone to blockage.
- (d) Need flame stabilisation detector to identify any flame on the flame trap surface, which could lead to burn-out of the trap.

BOX 16: Put to Drain

Solvent bearing effluents should not be put to drain; they should be sent to an appropriate effluent treatment plant.

Where disposal of miscible solvents to drain is unavoidable they should be diluted <1% v/v solvent content to render them incapable of forming flammable atmospheres.

Immiscible solvents should not be put to drain unless it is specifically designed to handle them with downstream treatment.

CONCLUSIONS

The discharge/disposal of relief streams is of increasing importance, the established practice of discharge direct to atmosphere being no longer acceptable, in many cases.

Consideration of discharge/disposal requirements should ideally be carried out as early as possible in the design stage, as part of a whole relief system.

The logic diagram provides a methodology to ensure that design of discharge/disposal of relief streams considers all the relevant SHE and other criteria.

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FIGURE 1 LOGIC DIAGRAM FOR THE SELECTION OF THE DISPOSAL SYSTEM

