TECHNICAL COMMITTEE FOR PLANT SAFETY (TAA)

at the
German Federal Ministry of Environment, Nature Conservation and Nuclear Safety

TAA - GS - 06

Guide

for the

Retention of dangerous substances flowing through pressure relief equipment

Status as of April 1994

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The Technical Committee for Plant Safety (TAA) is a committee constituted at the German Federal Ministry of the Environment, Nature Conservation and Nuclear safety under Section 31a of the Federal Immission Control Act.

Its registered office has been established at the premises of the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH.

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TECHNICAL COMMITTEE FOR PLANT SAFETY (TAA)

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Nature Conservation and Nuclear Safety

Guide for the Retention of dangerous substances flowing through pressure relief equipment

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The Technical Committee for Plant Safety decided at a special meeting on 18 March 1993 to draw up a guide with a list of criteria for the safe retention of dangerous substances flowing through pressure relief equipment depending on the hazard potential of the substances involved.

This guide was established, on behalf of the Technical Committee for Plant Safety (TAA) at the Federal Environment Ministry, by the study group on retention of dangerous substances flowing through pressure relief equipment.

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1 Introduction

This guide on the retention of dangerous substances flowing through pressure relief equipment is based on requirements of immission control law as defined in the Federal Immission Control Act and are in close relation with the Guide for the Identification and Control of Exothermic Reactions.
Where pressure relief is part of the safety concept of an exothermic reaction, it must be ensured that dangerous substances to be discharged from the reactor pressure system during pressure relief do not represent a hazard to man or the environment.

Dangerous substances with the exclusive characteristics:

1. explosive
2. oxidising
3. extremely flammable
4. highly flammable
5. flammable

will not be considered for our purposes, since these substances do not have a direct impact on man or the environment.

This guide is a summary of relevant knowledge and proven practices of the chemical industry and of the various institutions dealing with issues relating to safety of chemical reactions.
The guide identifies the measures to be taken for the retention of dangerous substances and specifies the conditions under which a direct and safe discharge of these substances into the environment is possible.
In this context, reference is made to section 3.4 of the latest version of TRB 600 on the installation of pressure vessels.

2 Scope of Application

This guide applies to installations subject to licensing pursuant to the Appendix of the 4th Ordinance for the Implementation of the Federal Immission Control Act in which pressure vessels with pressure relief equipment where chemical reactions take place are integrated.

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3 Definitions

Within the meaning of this guide, the following definitions apply:

Retention measures:

- e.g. the collection, accumulation, separation, storage and condensation in closed collecting systems;
- the transformation into harmless substances, e.g. through combustion in flares;

Dangerous substances:
Substances or substance mixtures (preparations) pursuant to Art. 3 a of the Chemicals Act and to Annexes II, III and IV of the Hazardous Incident Ordinance which show one or more of the following characteristics:

6. very toxic
7. toxic
8. harmful
9. corrosive
10. irritant
11. sensitising (?)
12. carcinogenic
13. teratogenic (toxic for reproduction)
14. mutagenic
15. other chronically damaging properties
16. dangerous for the environment

Pressure relief equipment:
Equipment which automatically prevents the exceeding of admissible operating overpressure by discharging substances.

4 Overall concept and general principles

Pressure relief equipment is the last link in a chain of measures to prevent the exceeding of admissible operating overpressure levels for a pressure vessel. In accordance with current regulations, pressure relief equipment must not be used for any control functions. Response

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from pressure relief equipment must be avoided wherever possible and is a very rare event.

If pressure relief is necessary, the decision on how the requirement of retaining the dangerous substances can be met should be preceded by an analysis of the individual case.

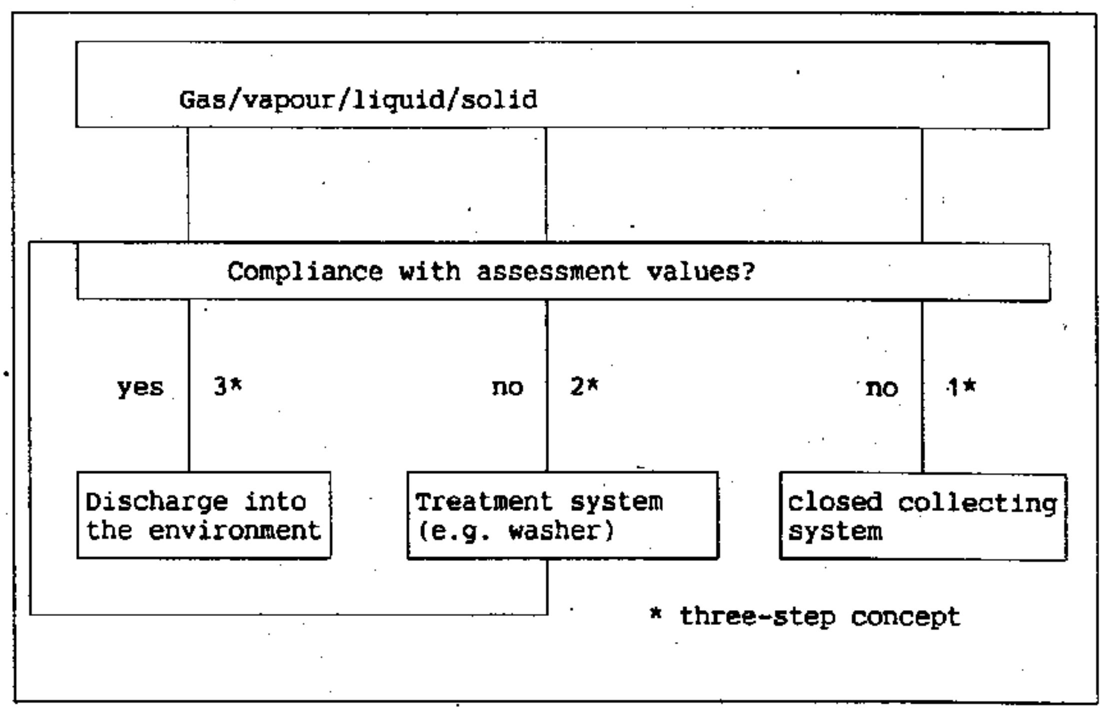
Such an analysis must take into account the installation's specific conditions of release as well as the conditions of propagation at the site in question.

Depending on the result or assessment of an individual case analysis, the safe discharge or retention should be based on the following three-step concept:

1. Retention by closed collecting systems

2. Retention by treatment systems (i.e. separator, flare)

3. Direct discharge into the environment



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Labelling in accordance with the Ordinance on Hazardous Substances	Qualifying quantity* (in kg)
very toxic (T+)	200
toxic (T)[1]	2.000
harmful (Xn)	2.000
corrosive (C)	750
irritant (Xi)	750
dangerous for the environment (N)	2.000

1 with the exception of carcinogenic substances, which will be treated as follows:

Pursuant to	Qualifying quantity (in kg)
Art. 15 a (1)	0
Annex I no. 1, 1.4.2.1.Kat. 1	20
Annex I no. 1, 1.4.2.1.Kat. 2	200

of the Ordinance on Hazardous Substances

* The reference quantity for the qualifying quantity is the content of the vessel made safe by the pressure relief equipment taking into account the type and quantity of the substance to be released.

The qualifying quantity for the individual substances listed in Annex II of the Hazardous Incident Ordinance is one tenth of the quantities specified in column 1 of this Annex.

5 Procedure for individual case analysis

The procedure for individual case analysis may be subdivided into the following processing steps:

5.1 Determination of the safety-related parameters of the substances

The characteristic values for the hazard potential of chemical reactions are described in the Guide for the Identification and Control of Exothermic Reactions.

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5.2 Determination of the mass flow blown out at opening of pressure relief equipment and of the total quantity released

The basis for the determination of the potentially released quantity is an analysis of the interaction, under failure conditions, between properties of individual substances and mixtures, and the process and operating parameters of installation components.

5.2.1 Determination of the maximum mass flow to be removed in the design case

To determine the design case, a closed volume, either in the intended use or due to a fault, is assumed for the pressure vessel, and it is analysed whether the input of mass and/or of thermal energy can result in inadmissibly high levels of pressure. With regard to the substances, the limited compressibility and the vapour pressures, which go up as temperatures increase are of importance.
Depending on overall conditions in the individual case, the design cases may, in principle, be subdivided into four groups.

5.2.1.1 Pressure increase caused by a pump or compressor

Mass flow can be determined by using the perforance curves of pumps or compressors.

5.2.1.2 Overflow from a higher pressure level

This refers to the overflow through open energy channels, the failure of reduction and pressure retention valves or an internal leakage resulting from inadmissible material strain. In such cases, the mass flow is produced by the pressure difference and the flow area.

5.2.1.3 Heating up from a higher temperature level

In these cases, the vessel volume is heated up using either direct heat flow in the form of mass or indirect heat flow transferred using a heat exchange area.
To determine the mass flow to be removed, the quantity of heating medium introduced and the energy balance are used.

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ad 1) If operative treatment systems (e.g. separators, flares) are unsuitable due to their limited capacities or similar technical limits, closed collecting systems can be used. These are sophisticated installations specifically designed for the retention of dangerous substances flowing through pressure relief equipment.

ad 2) In some of the operative facilities, used in continuous operation, substances can be treated, depending on their properties, by means of dissolving, condensation, combustion or chemical reaction. It must be assessed whether the immission loads emanating from the non-retained residues are tolerable.

ad 3) The qualifying quantities specified in the table below are intended to provide assistance in taking the decision on the necessity of a treatment or retention system. The qualifying quantities have been selected in such a way that a treatment or retention system is normally necessary when they are exceeded. If the individual case analysis provides proof that the possibility of generating a serious danger within the meaning of the Hazardous Incident Ordinance is precluded because measured values are below recognised assessment values for soil, water and air (e.g. the ERPG-2 value), a direct discharge of the substances blown out in the environment may be tolerated.

With regard to requirements for official controls, it is recommended to require submission of the results of individual case analyses if the qualifying quantities set out in the table below are exceeded, provided that no treatment or retention systems are planned.
If the quantities are below the qualifying quantities, it is recommended, in usual cases, not to require submission of the results of individual case analyses.

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5.2.1.4 Pressure increase resulting from material transfer

Measures to be taken in extreme cases involving chemical reactions normally require a particularly extensive analysis based on detailed investigations involving laboratory equipment. The Guide for the Identification and Control of Exothermic Reactions provides the necessary advice and describes the procedure for the definition of a safety concept.

If pressure relief including safe retention or safe discharge is integrated in the safety concept as a limiting measure after the failure of upstream measures to prevent the feared event, the design case must be clearly characterised.

Example: Failure of the cooling system of a batch reactor in which the design quantities safeguarded by organisational and technical measures have been added.

For the design of pressure relief, e.g. the following prerequisites must be fulfilled, and/or the following data be provided:

- clear correlation between temperature and pressure (set pressure);
- sufficiently high vapour pressure (set pressure > normal pressure);
- sufficient quantity of evaporable substances for the purpose of cooling by boiling;
- substance properties such as propensity to expansion and higher viscosity may result in an escape in two phases;
- heat production rate dQ_R/dt and/or gas formation rate dM/dt at the temperature corresponding to the set pressure;
- the function of the pressure relief equipment must not be affected by excessive polymerisation, conglutination or corrosion.

For the relieve of a reactor, a sufficiently large quantity of vapour mass flow, depending on the heat production rate, must be blown out of the reactor. In addition, a gas mass flow must be discharged depending on the gas formation rate. When dimensioning the pressure relief area, both mass flows must be taken into account.

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5.2.2 Dimensioning the relief area taking account of upstream and downstream parts of the installation (pipings)

Depending on the physical condition of the substances within the mass flow, or the splitting into gaseous or liquid portions, the calculation of the pressure relief area is carried out on the basis of different calculation methods:

- one-phase gas/vapour or fluid flow using the laws of fluid dynamics;
- assessing whether two-phase escape occurs, on the basis of the substance properties (surface tension, viscosity) and the phase separation conditions (gas velocity[1], filling level in the vessel) using a phase separation model (e.g. DIERS diagramme);
- multiphase escape through mass flow and pressure loss models (empirical approaches, the results of which have been proven by tests). Pressure relief test benches are available in particularly difficult individual cases.

In the following, some of the influences of upstream and downstream installation parts (pipings) have been listed which may reduce the blow-out capacity of the pressure relief equipment and must therefore be taken into account with a view to dimensioning the pressure relief area.

- pressure loss in the supply line;
- pressure loss in the blow-out line;
- pressure loss in the liquid separators and retention systems, increased back pressure on the pressure relief equipment due to the required condensing pressure in the retention system.

In this context, the process of determining the flow forces in the pipings (especially in the case of two-phase flows) must be mentioned.

As regards the dimensioning of pressure relief equipment, attention is drawn to the guide for dimensioning the flow areas of safety valves

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1 in relation to the vessel cross section

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and rupture disks, which is at the moment being drawn up by a group of experts representing both industry and scientific institutions.

5.2.3 Determination of the total quantity released at opening of pressure relief equipment

As a result of the selection of the pressure relief equipment (rupture disk or safety valve) and the definition of the pressure relief area, the blow-out process is unambiguously characterised with respect to mass flow.

On the basis of an energy or mass balance, the mass flow released over time and the total quantity thus blown out, or the duration of the process, may be determined for chemical reactions or for pressure relief processes that are fed by a limited energy and mass reservoir located outside the vessel.

In the case of pressure relief processes that are triggered by a pressure generator (e.g. a pump) or an energy source (e.g. superheated vapour supply), the total quantity is critically influenced by the time at which these sources are switched off through organisational or technical measures.

5.3 Specification of the conditions for the blow-out from pressure relief equipment

Once the evolution of the mass flow over time and thus the total quantity blown out as well as the properties of the substances blown out are known, it is time to specify the conditions for the blow-out with regard to the following:

- physical condition of the substances;
- place, direction and height of the outlet;
- impulse of the outlet flow (direction, speed);
- factors relating to the surroundings (vicinity, water bodies, built-up areas etc.).

The physical condition of the substances is relevant with a view to assessing the blow-out process in two different respects. For the gas-

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eous part of the mass flow, the mixture with ambient air must be monitored, and the propagation calculated. For the liquid part, it must be determined where the liquid splashes or is sprinkled (possibly on the roof of the building) and what mass flows volatilise or evaporate from the liquid released. Depending on the hazard potential, a decision on the separation and collection of the liquid phase may become necessary at this stage.

The place of blow-out is of particular importance for the turbulent mixing of the quantities of gas blown out and thus for dilution in the atmosphere. Therefore, the place of blow-out chosen should be located as far as possible above the building housing the installation.
In the near vicinity of the place of blow-out, the hazard can be minimised by choosing to direct the release to areas not under risk (e.g. on the works premises).

Inly in the vicinity of the outlet is the impulse of the outlet flow of great importance for the dilution of the substances released. A turbulent free jet allowed to develop unhampered leads to a rapid initial dilution, so that even the blow-out of gases with a specific weight higher than that of air does not entail any heavy gas effects.

Apart from an increase in the effective height of release in the case of a vertically upward outlet, the propagation of a free jet has no major impact on immission loads at distances of more than 100 m.

If, at a close range, no turbulent free jet is formed, or if an accumulation of heavy gases occurs as a result of the volatilisation or evaporation from a liquid spill, a propagation of heavy gases must be assumed. This applies all the more, the closer the place of blow-out is to ground level.

In order to determine the place where a possible hazard for man and the environment may occur, the surroundings of the place of blow-out must be investigated. This includes, if applicable, the surroundings of the installation on the works premises as well as the endangered zones (e.g. buildings, water bodies, soil) outside the works premises.

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5.4 Determination of the concentration and duration of the impact in characteristic places

With the aid of recognised propagation models for the description of free jet propagation or atmospheric propagation (see VDI 3783), the evolution over time of the concentrations of the substances emitted can be calculated for the air path, depending on the distance to the pressure relief equipment.

The following data are essential for the calculation of VDI 3783:

- mass flow over time or, in the case of spontaneous release, the total quantity;
- height at which the blow-out occurs, altitude and distance of the point of contact with the earth, the surroundings (built-up areas, topography) characterised by "soil roughness categories";
- weather situation (turbulence rate of the atmosphere) characterised by propagation categories (stable, unstable and indifferent propagation situations), taking into account possible inversion layers;
- wind velocity.

On the basis of the time dependent mass flow determined, a continuous point release (including, if necessary, the formation of a free jet) is simulated, or, if the period of emission is short (considerably lower than the quotient of distance from the contact point and wind velocity), a spontaneous point release of the total mass is simulated.

If the release takes place at a point high above the installation, and if places at a distance of more than 100 m are to be investigated, a density neutral release of gas can as a rule be assumed. The application range of these propagation models is limited to distances of more than 100 m. If shorter distances are taken, immission prognoses are subject to a higher degree of uncertainty, due to model characteristics. In the vicinity of the point of blow-out, a free jet propagation or a heavy gas propagation can be assumed, depending on the invidual case.

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With regard to the atmospheric propagation pursuant to VDI 3783, the turbulence rate of the atmosphere, which develops depending on the vertical temperature gradients in certain weather conditions, is defined by three propagation categories (stable, unstable and indifferent).

Normally, an inversion layer is assumed to exist at a level of 20 m. At large-scale industrial facilities, however, a considerably higher inversion layer (up to 100 m) may be assumed due to thermal characteristics.

For a height of blow-out of more than 20 m, it is assumed that the emission is reflected from a blocking layer at the level of the point of blow-out.

Taking into account the categories of roughness for the modelling of "unevenness" of the surroundings such as built-up areas or vegetation, the immission load at the contact point is calculated for the three propagation categories with an assumed wind velocity of 1 m/s and assuming the existence of an inversion layer. The most unfavourable result of these three calculations (i.e. the highest immission load) thus characterises the most unfavourable propagation situation, which only rarely occurs simultaneously with the blow-out from pressure relief equipment, and is used for the assessment of the hazard.

In justifiable exceptional cases, a mean propagation situation with indifferent weather conditions without a blocking layer and with a wind velocity of 3 m/s is assumed, and thus, the immission load is determined for frequent propagation conditions.

If, in the case of a blow-out, a significant part of the liquid is released, the liquid which is distributed into the atmosphere in the form of drops and volatilises, evaporates or is sprinkled must be taken into account for determining the immission load. For this purpose, assumptions must be made about drop size, drop distribution as well as the volatilisation or evaporation rate.

Flowing period models (e.g. the Rhine Model) can be used to determine the evolution of concentrations in surface waters.

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5.5 Assessment values

In order to answer the question of what is the substance quantity that must be released to present a hazard for man and the environment at the contact point, substance-specific assessment values are needed. Since the blow-out from pressure relief equipment generally involves operations that last for a short period of time only (several minutes), these assessment values must primarily refer to acute, short-term hazards. Apart from concentration levels, the duration of impact is of major importance.

At the moment, there are no uniform and generally recognised assessment values yet. With regard to human toxicology, the ERPG-2 values should, where available, be used for the assessment of the discharge of dangerous substances, based on the discussion results of the Hazardous Incident Commission.

Where no recognised assessment values are available to assess the hazards of long-term effects of short-term exposure, assessment must take place on a case-by-case basis in consultation with experts.

As regards the water path, a first assessment of possible hazards for the environment can be made using the classification method applied by the International Commission for the Protection of the River Rhine in the case of accidents resulting in damage to water bodies.

6 Safe discharge or safe retention of substances flowing through pressure relief equipment

The following three-step concept can be used to meet the requirements of immission control law and to be in line with the state of the art of safety technology applicable to hazard-free discharge:

- retention by closed collecting systems;
- retention by treatment systems (e.g. separators, flares);
- direct discharge into the environment.

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6.1 Retention by closed collecting systems

6.1.1 Closed space for collection

Can be used for liquids, solids and gases/vapours.

Please note the following:
- the mass that can be collected is limited, especially with gases/vapours (otherwise large volumes are needed);
- the resulting pressure influences the pressure relief equipment.

6.1.2 Closed collecting system with upstream immersion facility

Pipe manifolds or jet condensers can be used for
- condensable vapours;
- gases easily soluble in gaseous form in the liquid of the upstream immersion facility;
- substances to be chemically neutralised or transformed in the liquid of the upstream immersion facility (e.g. chlorine in sodium hydroxide);
- if necessary, they are also suitable for the lower, liquid content of a two-phase flow if the pressure difference is tolerable for the distribution;
- if necessary, safe disposal of the non-condensable/non-soluble parts in a downstream flare/TAR (necessary especially for major quantities of inert gas).

Please note the following:
- the condensation rate ("efficiency factor") increases with the quality of vapour distribution, the decrease in the temperature of the cooling agent used and the reduction of the quantity of inert gas;
- the pressure used to condense the substances should be sufficiently low (since it has an impact on the compressive strength of the equipment and on the back pressure bearing on the pressure relief equipment);
- pressure losses caused by distribution systems, feeder lines and the depth of immersion have an effect on pressure relief equipment;

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- measures of measuring and control technology to guarantee that conditions are in line with assumptions made for the design: e.g. monitoring devices including alarm for filling levels and temperatures;
- if necessary, heating for outdoor facilities (antifreezing) or cooling of the liquid to be used.

6.2 Retention by treatment systems

In some of the operative facilities, used in continuous operation, substances can be "disposed of" by means of dissolving, condensation, combustion or chemical reaction, depending on their properties. With a view to the suitability and selection of one of the alternative processes, a number of generally valid criteria need to be considered, including the following:

- examining the capacity concerning the mass flow and total quantity blown out;
- considering the effects of pressure loss in the pipings and in different pieces of equipment on the pressure relief equipment;
- ensuring that the relevant path cannot be closed up;
- examining the corrosive strain on the materials.

The suitability of the alternative systems regarding the retention of substances as well as their limits of application or, if necessary, relevant criteria will be described in the following.

6.2.1 Separator (filter) or collecting container (catch tank)

Can be used for
- liquids;
- two-phase (or three-phase) mass flows with separators (or filters) and with collectors for the liquids (or solids) and with collectors for gases/vapours in downstream operative facilities such as washers, flares/TAR or A-carbon towers, or retention of gases and vapours in closed collecting systems, if applicable, with upstream immersion facilities.

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6.2.2 Washers and upstream immersion facilities

Can be used for all types of gases and vapours, combustible, toxic, very toxic or carcinogenic, which are

- soluble or
- neutralisable or
- condensable by using a cold cleaning solution or
- chemically absorbable.

Please consider the following:

- What are the effects on the waste water of the washers? Does separate disposal become necessary?
- Is the washing liquid suitable for the substances to be retained?
- Can undesired reactions with the washing liquid occur in the washer (i.e. compatibility of the substances)?

6.2.3 Flare/thermal waste gas purification (TAR)

Can be used for

- combustible gases/vapours;
- toxic, very toxic or carcinogenic substances, insofar as they are thermally decomposable/combustible and the combustion gases formed present no hazards.

Please consider the following:

- Is the flare or TAR designed for possibly high short-term exposure levels, i.e. might it not be extinguished, or is there not the possibility of a bypass, due to the excessive exposure levels?
- Will the classification of explosion zones for the waste gases which are to be burnt in the flare/TAR change as a result of the input of the combustible substance, i.e. are effects regarding backflash etc. possible? Can other effects on the connected installation parts be excluded?
- Since the feeder lines are usually long, the loss of pressure on the pressure relief equipment must be examined separately.

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6.2.4 Activated carbon systems

Can be used for all types of gases or vapours which can be linked by absorption to A-carbon.

Please note the following:

- assessing the hazard potential concerning possible oxidisation or decomposition reactions (A-coal burning);
- disposable mass flow or total mass is very limited.

6.3 Direct discharge into the environment

The existing operative safety concept, the installation-specific conditions of release and the specific propagation conditions at the site can be used to evaluate, on a case-by-case basis, the risks that may occur during the blow-out from pressure relief equipment outside of the installation.

If the results of these case-by-case examinations fall below the level of recognised assessment values, a direct discharge into the environment of the substances blown out can be tolerated.

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