



P E R O X Y G E N S

HYDROGEN PEROXIDE Subgroup

BULK STORAGE

GUIDELINE

(September 2001)

Chemistry making a world of difference

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H₂O₂ BULK STORAGE GUIDELINE

PREFACE

September 2001

The guideline has been developed by a task force led by ATOFINA comprising: of the following Companies:

ATOFINA SA
AUSIMONT SpA
EKA Chemicals AB
KEMIRA Chemicals OY
F M C Foret SA
DEGUSSA AG
SOLVAY SA

From the start of this project the task force has benefited from the guidance and helpful comments of Mr Bertil Lindeberg of the Swedish Rescue Services Agency who could express the concerns of the competent authorities and present the views of regulators.

The development of this guideline is in accordance with our Responsible Care commitment to all stakeholders throughout the life cycle of Hydrogen peroxide. Its purpose is to provide a single authoritative source of guidance for controlling the risks of bulk storage which is intended to be widely available to all stakeholders. It is the policy of our companies to achieve the standards embodied in the guidance.

The document is maintained by the Technical Committee of the CEFIC Hydrogen Peroxide sub group, the updated version can be found on the CEFIC website.

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PURPOSE AND SCOPE OF THE GUIDELINE

“The chemical industry aims to play a leading role in the management of chemicals. It considers that it is industry’s responsibility, in partnership with the authorities and other stakeholders, to ensure that its chemicals are safely produced, used and disposed” – Chemical Management : a CEFIC initiative, March 1999. This guideline on the BULK STORAGE OF HYDROGEN PEROXIDE is an illustration of this commitment of CEFIC.

End-uses of hydrogen peroxide (HP) have undergone major development during recent decades : more than two millions tons 100% of HP are used world-wide in multiple applications, principally based on the oxidizing properties of this product. Recognised as environmental friendly in so far as its by-products, water and oxygen, do not represent any risk, HP remains nevertheless a chemical for which storage and handling are safe only as long as strict safety principles are known and respected by all.

The European producers of HP, members of the CEFIC peroxygen group, have decided to combine their knowledge and experience in order to present consistent recommendations on the bulk storage of HP. The purpose of this guideline can be defined as following :

- To provide to users, authorities and other stakeholders information for carrying out risk assessments for new or existing storage installations of HP. Although HP is a well-known product, the existing literature on the product is wide but neither complete nor homogeneous. This guideline, as a common source of information, should minimise the risk of confusion and uncertainty among producers, users and regulators.
- To ensure the safety of the installations of producers and users of HP by realistic proposals concerning the design and operation of HP storage installations. This guideline should be used as a basis for training and increasing the know-how of all HP users.
- To set up minimum harmonised requirements for the storage installations, accepted by all the HP producers members of the CEFIC.

The scope of the guideline is restricted to the following installations :

- Concentration of HP up to 70%. Higher concentrations of HP present other potential risks (e.g. self explosion risk) and are only used in small quantities for minor and specialised applications.
- Fixed storage installations of HP. The transportation, packaging and uses of HP are not covered in this guideline.

Considering the diverse nature of existing HP storage installations (different concentrations of product, different size and location of the tanks), it is impossible to define fixed technical and organisational standards having to be used in all cases. Our methodology for the development of this guideline has consisted of providing a risk assessment framework and the main basic elements for

- the design of the HP storage tank and its auxiliary equipment,
- the definition of the operating procedures related to the HP storage installation,
- the preparation of the emergency plan,

in order to reach the best level of safety for the personnel and the environment by the introduction of best practicable means.

This guideline reflects our present best level of knowledge. It is not intended to replace the applicable regulations but is complementary to them. The common commitment of the CEFIC HP producers is to maintain an improved HP safety through the implementation of this guideline. All of these companies are ready to help all stakeholders in the achievement of this objective.

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DEFINITIONS

For the purpose of this guideline, the following terms are defined below :

Adequate : this term is used in the risk assessment of the chapter 3. It refers to the effectiveness of safety features in preventing harm to people and environment and material damage, given the present state of the art of the European producers.

Best practicable means : the techniques by which the greatest reduction of risk is obtained, taking into consideration the economic aspect.

Concentration : the concentration in percent of HP in this guideline always refers to weight concentration.

HP : commercial aqueous solutions of hydrogen peroxide, with a concentration up to 70 %.

Incompatible material : a material that, when in contact with HP, can cause hazardous reactions such as decomposition or is itself adversely affected by contact with HP.

Minimum requirement : indicates that the item in question must be incorporated at every HP storage installation according to the current guideline. Should technical or organisational alternative be chosen, it has to be demonstrated that it brings a comparable level of safety.

New installation : indicates a new site that includes a HP storage tank.

New storage tank : indicates a new HP storage tank, that nevertheless may be installed in an existing site, with existing constraints regarding the location which have to be taken into consideration in the study of the best practicable solution.

Shall : indicates a mandatory requirement.

Should : indicates a recommendation or that which is advised but not mandatory.

Storage tank : a storage tank in this guideline refers to the fixed tank used for the storage of HP as commercial solution (tank of final product for the producers, tank of raw material for the users). The storage and handling of drums or IBC is not covered in this guideline.

Recommendation : indicates advice, the application having to be considered in the context of each installation.

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1. PROPERTIES AND CLASSIFICATION

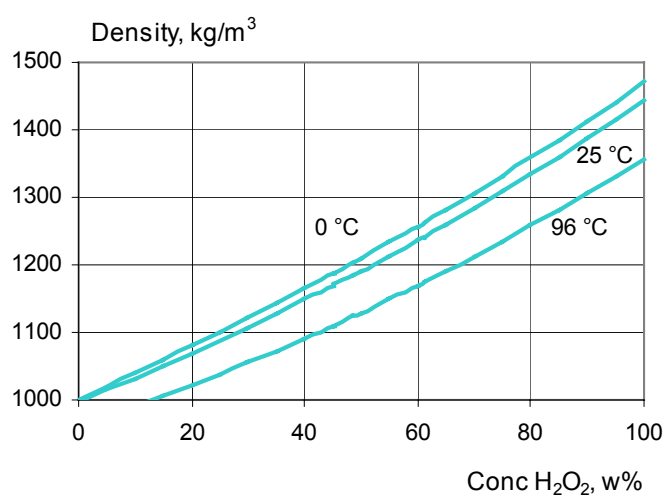
1.1 Physical datas and properties

HP is a clear, colourless liquid. It is only used in aqueous solution and is miscible with water in all proportions. At low concentrations, HP is odourless. It has a slightly pungent odour at higher concentrations.

Chemical formula: H₂O₂. Molecular weight 34.016

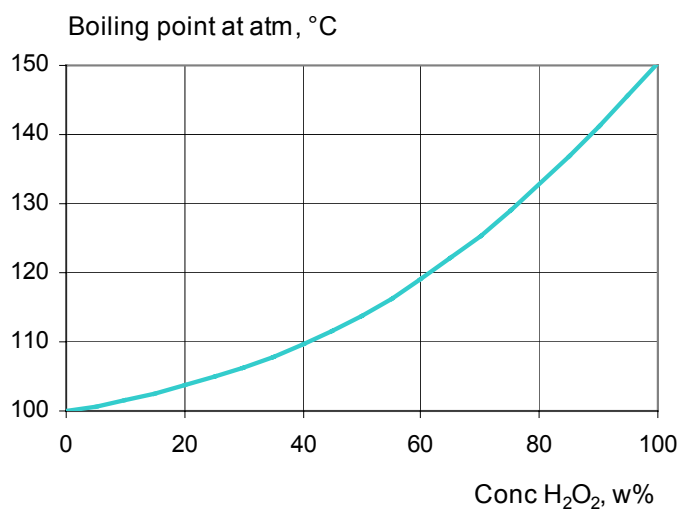
DENSITY

The density of HP at different temperatures.



BOILING POINT

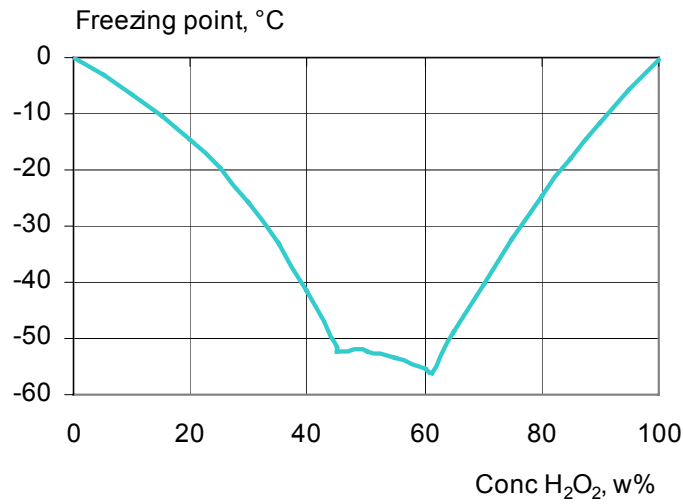
The boiling points of HP at atmospheric pressure.



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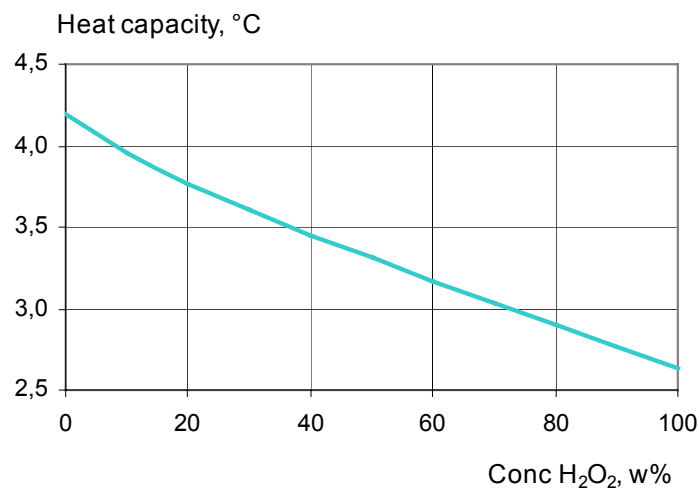
FREEZING POINT

HP at various concentrations have the following freezing points.



SPECIFIC HEAT

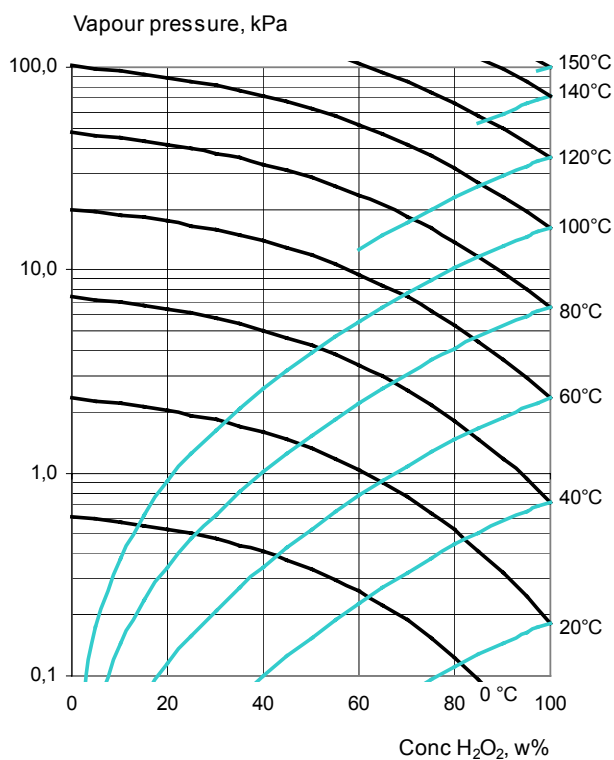
The specific heat of HP at 25 °C.



VAPOUR PRESSURE

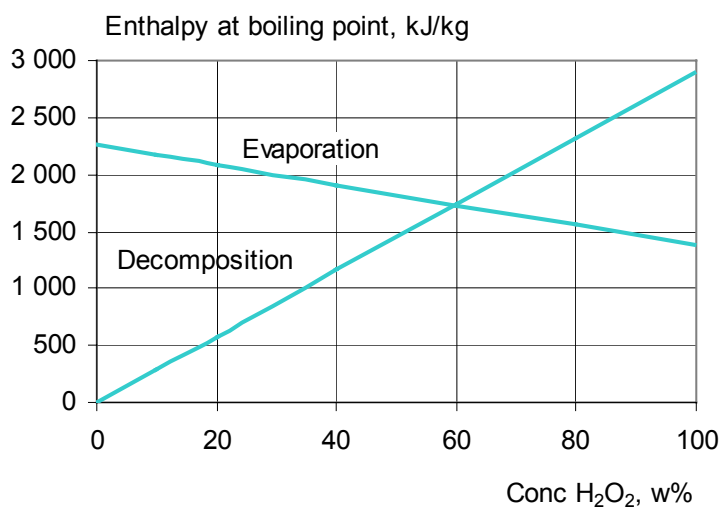
The total vapour pressure (black curve) over an H₂O₂ increases with increasing temperature and decreases with increasing H₂O₂ concentration. The partial pressure of H₂O₂ (blue curve) increases with increasing temperature and the H₂O₂ concentration of the solution.

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HEAT OF EVAPORATION

Transformation of HP to vapour requires less heat at high concentrations of H₂O₂.



Comment : Calculations and tests confirm that there is always a decrease of the concentration of the HP in case of adiabatic decomposition, even for concentration above 64%¹.

Physical properties of typical HP :

¹ (1) Test report Eka Chemicals BC 2001-116

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Concentration weight %	Density 20 °C kg/m ³	Boiling point °C	Freezing point °C	Viscosity	
				Ns/m ²	cp
0 (water)	1000	100	0	0,001002	1,002
35	1132	108	-33	0,00111	1,11
50	1196	114	-52	0,00117	1,17
70	1288	126	-40	0,00124	1,24

1.2 Chemical data and properties

HP is a very reactive substance and can undergo different types of reactions based on the following chemical mechanisms :

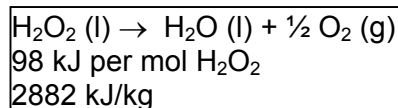
- decomposition,
- redox reactions,
- reactions with organic materials.

Incompatibility with substances and materials should **always** be assumed unless the opposite has already been proven.

DECOMPOSITION

In its commercial form, HP is a stable compound. pH of industrial peroxide is controlled by producers in order to ensure a maximal stability of the HP. Decomposition occurs when HP is contaminated by e.g. metals.

Decomposition is affected by heat, pH and contamination. HP forms oxygen and water upon decomposition. The reaction generates heat, which may be substantial.



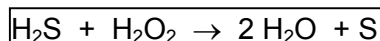
Impact of pH : both decrease and especially increase of the pH can have a negative impact upon stability. If the pH of the HP is raised, this considerably increases the rate of decomposition. This may occur when alkaline substances (e.g. caustic soda, sodium silicate, lime, hypochlorite, ammonia) are mixed with HP.

Homogeneous decomposition : accelerated decomposition may occur when HP is contaminated with incompatible soluble substances, even when the level of contamination is low (a few ppm). This is called homogeneous decomposition and occurs with a wide range of contaminants, especially salts of e.g. copper, chrome, iron, vanadium, tungsten, manganese, molybdenum and platinum.

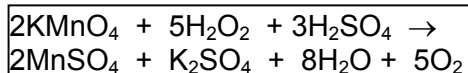
Heterogeneous decomposition : heterogeneous decomposition is the occasionally very rapid decomposition of HP which occurs when it comes into contact with insoluble material. This occurs on contact with almost all material, but the speed of the decomposition varies greatly, depending on the nature of the contaminant and its contact surface.

REDOX REACTIONS

HP has a high oxidation potential and acts as a powerful oxidizing agent. Hydrogen sulphide dissolved in water is oxidized, eliminating, for example, evil-smelling hydrogen sulphide from waste water.



Under certain conditions, HP may also act as a reducing agent, for example in the following reaction with potassium permanganate. The reaction may be used to determine the concentration of HP.



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REACTIONS WITH ORGANIC SUBSTANCES

HP generally acts as oxidizing agent in degrading many organic compounds. At low concentrations, these reactions are slow and safe. When HP concentration exceeds 30% (in the mixture) however, homogeneous mixtures of HP and organic solvents can become explosive.

At concentrations below 30%, HP in contact with other chemicals are capable of forming dangerous substances (for example organic peroxides).

1.3 Classification and Labelling

Classification according to Annex I of Directive 67/548/EEC

HP \geq 60 % (by weight)

Classification: oxidizing and corrosive

Labelling:	Symbols:	O	Oxidizing
		C	Corrosive

HP $20\% \leq c < 60\%$

Classification: corrosive

Labelling:	Symbol	C	Corrosive
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HP $5\% \leq c < 20\%$

Classification: irritating

Labelling:	Symbol	Xi	Irritating
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2. HAZARDS AND CONSEQUENCES ASSESSMENT

2.1 Hazards

The potential hazards associated with a peroxide storage installation may be classified as follows :

- Decomposition, leading to
 - vapour release
 - pressure burst (if venting is inadequate)
- Loss of containment, leading to
 - fire
 - environmental and health hazards

Both vapour and condensed phase explosion hazards associated with HP alone (not contaminated by organic materials) do not have to be considered in the case of bulk storage of usual concentrations below 70 %.

2.1.1 Decomposition

There is always with HP a so called natural decomposition which is easy to handle (the product must never be stored in a totally closed environment).

Considering a tank submitted to a higher rate of decomposition, it will release and disperse oxygen, steam and HP fumes. The rate of release is variable, depending on the prevailing decomposition or boil up rate while the total quantity released is depending on the initial inventory and HP concentration.

Decomposition may be initiated by an increase of temperature due to an external heat source (see §2.1.3) or by catalytic contaminants such as transition metal ions, strong acids or bases.

A convenient method of classifying all potential sources of contaminants is to assign each to a level of catalytic activity, representing a decomposition rate increase of say 100, 1000, 10 000 times the normal. The effect of particular contaminants can vary enormously depending on their nature and amount, the stabilisation of the product and other factors. Some typical values are shown in appendix 1 (experimental results with addition of iron or caustic soda). Based on experience, the contamination with alkaline products represents the most critical scenario of decomposition to be considered for HP storage tanks.

In order to obtain rate increases of 100 times or greater, it is necessary for the peroxide solution to become grossly contaminated which should not normally be possible in a well maintained storage. In such a case, any increase in the rate is expected to come from a natural build up of metal ions due to corrosion/erosion (especially in small tanks) or by the loss of the effectiveness of the stabilisers. In these circumstances, the increase in rate will typically range from 10 to 100 times the normal. This suggests a 100 fold increase in the rate is a realistic maximum for catalytically induced decomposition and a value of 1000 probably representing a conservative value for the design of the safety vent. In case of extreme contamination (e.g. alkaline), a higher rate can be anticipated.

A progressive decomposition may lead to safe venting of the resulting gas and vapour, or a pressure burst of the vessel if the vent is not adequate. In the case of the former, the only consequence will be that arising from a harmful peroxide vapour emission and the subsequent risk of exposure. In the event of a pressure burst, there could be additional effects due to blast, missiles or hot liquid ejection.

2.1.2 Loss of containment

Fire hazard

HP and its oxidising properties could cause fire in the presence of organic substances or other combustible materials (wood, paper, textiles, leather, ...). In the presence of H₂O₂, the intensity of a resulting fire will be greatly enhanced. Be aware that fire may not start immediately due to the slow temperature increase but can occur after a delay.

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Health hazard :

HP poses risks to human health. It is irritant to the eyes and skin at concentrations above 5% and causes burns above 20%. In the event that HP is swallowed, it can be harmful with increasing risk of serious injury or fatality with increasing concentration.

HP is not classified as a carcinogen.

Inhalation of the vapour or mist will cause extreme internal irritation.

Occupational exposure limits :

- Time Weighted Average (8-hour): 1 ppm (1,4 mg/m³),
- Short Term Exposure Limit (15 min): 2 ppm (3 mg/m³).
- Immediately dangerous to life or health concentration (IDLH): 75 ppm (105 mg/m³)

Environment hazard :

HP occurs naturally in the environment at levels of 0,1 – 4 ppb (air) and 0,001 – 0,1 mg/l (water).

Air: there is no regulatory limit industrial emission to air.

Water: HP is a substance which can be rapidly degraded but also has the potential to kill microorganisms and higher species. Laboratory studies have shown that algae are the most sensitive species and the predicted no effect concentration is 10 ppb.

Soil: HP decomposes readily to form water and oxygen

2.1.3 External fire, vapour and condensed phase explosion

These scenarios are not considered later in the guideline for the following reasons:

Vapour or condensed phase explosion of HP itself is impossible for concentrations below 74% : it is therefore excluded from this guideline.

For other explosion scenarios, a precondition is the presence of organic material in the HP installation. This precondition is generally avoided by the design and operating practises of an HP installation. In particular, there is a strong focus on the avoidance of all contamination and incompatible materials including organic materials.

In principle, a mixture of HP and organics can lead to a condensed phase explosion for HP concentrations over 40% and under special conditions (miscibility, concentration and dispersion of the organics). Such an explosion releases an enormous quantity of energy (detonation), so that no safety relief equipment could prevent a burst of the tank. For plants having to deal with this risk, special emphasis on prevention must absolutely avoid organic contamination. The following requirements apply in such a case :

- segregation from organic materials for storage and drainage,
- procedures should be established that exclude absolutely the possibility of unloading an organic material in an HP peroxide tank, and vice versa (separated lines, double locked system, procedure of access control).

For fire, the effects on HP are likely to be minimal; the worst being a remote chance of bursting a pipe. Only small tanks (and especially plastic tanks) could be affected within a reasonable time-scale ; a specific protection of the tank should be studied in such a case. Bigger metallic tanks (> 50 m³) can stand a fire for several hours because of the small exposed surface area/mass unit (past incident experience is consistent with this view).

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2.2 Assessment of Probable Consequences²

2.2.1 Decomposition

Release and dispersion :

One of the consequences of a peroxide decomposition is the release of potentially harmful vapours into the atmosphere. It is therefore necessary to determine dispersion characteristics so that the ground level concentrations can be estimated and compared with the maximum allowable for exposure to give a contour of affected distances. The best available method is a computer based model. The source term for such a model includes:

- rate of release,
- duration/quantity of release,
- its temperature (and pressure) on release.

For a catalytically induced decomposition, calculations suggest the quantity of peroxide vapour released (Ci = 70%) remains constant at about 60 kg H₂O₂ vapour/ton of product, the duration of release varies in the range of 3 to 300 min (0,2 – 20 kg/min/t of product) depending on the level of catalytic activity.

For a decomposition initiated by fire exposure, the rate of vapour evolution is relatively low (about 0,4 kg/min/t based on a 50 t tank) and may be assumed to be dominated by the selected decomposition case.

The vapour temperature on release is an important consideration in determining the initial rise of the plume since the further it rises, the lower is the chance for it to drift downwards at high concentrations.

The results of a simulation carried out using a recognised computer model for a vessel containing 200 t of 70 % HP undergoing a thermal decomposition at a rate of 100 times the normal suggest that the initial buoyancy of the cloud emitted through the vent is such that it rises very rapidly to 80 meters before it disperses as a buoyant plume. The dispersion behaviour of the cloud at two different meteorological conditions also shows that the Immediate Danger to Life and Health (IDLH) or Emergency Exposure Index (EEI) concentration is never reached at the ground level even though the cloud may drift in excess of several kilometers from the source of release.

A similar calculation with the assumption of a decomposition occurring at the ground level (decomposition in the safety bund) suggests that HP vapour with concentration above the IDLH may drift up to a distance of 300 meters away from the emission source (100 t of 70%, decomposition at a rate of 1500 times the normal).

The models take no account of droplets either from condensation of vapour or from emission at source or any subsequent decomposition that may occur in hot vapour. Although in principle, droplets may occur over a wide range, incident experience indicates that significant effects are not observed outside the immediate vicinity of the source.

Pressure burst :

Storage tanks must be provided with emergency relief vent designed to relieve at low pressure. In the event of a substantial decomposition, overpressurisation may occur leading to bursting of the vessel at or around its yield pressures. In these circumstances damage could result from air blast and emission of hot reaction products.

² CEFIC - Guidance note for the bulk storage of hydrogen peroxide – 1994

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Air blast :

In the event of an overpressure, a proportion of the released energy is always utilised to create the blast. This proportion is difficult to set because of different failure modes. In the absence of information on failure modes, no serious error is introduced if a value in the middle of the range is assumed (say 50%).

A method of estimating blast damage relies on the concept of TNT equivalence. Blast damage has to be considered in the immediate vicinity of an explosion and is usually weak (window breakage, light inner wall rupture,...) below the overpressure circle of 50 mbar. Missile effects beyond this overpressure limit have a low probability of occurrence. See example of calculation in appendix 3.

Liquid ejection :

It is not possible to quantify effects which may result from hot liquid/vapour ejection with any order of accuracy. However, it is not expected that these effects can extend to very great distances. Incident experience is consistent with this view.

2.2.2 Loss of containment

Fire:

If a fire occurs together with a leakage of HP, the HP decomposition and oxygen production will increase the intensity in burning. This increase will be translated into a greater fire growth and higher flame temperatures than if there were no oxidant present. An acceptable compromise for the estimation of this effect would be:

- a 50% increase in the flame height
- an increase of up to 100% in the surface emissive power of the flame to a maximum of ~250 kw/m².

Contact with human:

Damage to the eyes, skin in case of external contact ; damage to bronchia in case of inhalation. This damage might be irreversible or even fatal.

Environment:

Can cause short term damage. However the H₂O₂ is not persistent and the environment can fully recover.

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3. GENERAL GUIDELINES FOR STORAGE

The purpose of this guideline is to act as a reference source for informing all concerned on how to achieve an acceptable level of risk from bulk HP storage operations. The first step is to set the overall risk management framework.

For each of the major hazard scenarios (accelerated decomposition and loss of containment), there are in principle two stages during which damage to people, environment and material can be avoided. These stages are prevention, and control/damage limitation (C/DL).

The guiding principle - according to experience - is that, although the many elements of prevention are always necessary, they may not always be sufficient (a single defect in one element can be enough to initiate an incident). Therefore, for the overall level of risk to be acceptable, there must be additional effective C/DL measures.

In order to specify the extent of additional C/DL measures required, it is first necessary to explain the risk categorisation philosophy upon which this guideline is based.

Three categories are identified as follows:

- **Preferable:** This is the highest standard and is expected to result in the lowest risk. It should be considered as the specific target for new designs.
- **Acceptable:** This standard, whilst not as high as the above, is accepted for existing installations.
- **Unacceptable:** This standard represents an unacceptable risk to man and/or the environment and improvements have to be made.

In the following sections, both main hazards are considered in turn and in each case, the available combinations of C/DL measures are categorised as preferred, acceptable or unacceptable.

3.1 Hazards

3.1.1 Runaway decomposition

This event can occur if the rate of H₂O₂ decomposition is increased due to catalytic impurities. There are many possible sources and they must all be excluded for prevention to be successful. Common examples are :

- inappropriate materials of construction (vessel, pipework, fittings, equipment components...)
- ineffectively passivated material of construction
- external contamination (airborne, maintenance, cross contamination, misdirected chemical delivery)

The details of the necessary prevention measures for the above are given in later chapters. The following table sets the standards for C/DL measures. It is derived from an assessment of the risk of human injury resulting from either the bursting of inadequately vented equipment or exposure to vapour/liquid emanating from a runaway decomposition. Definition of adequate venting, separation and detection is given in chapters 4 and 5. A local supply of water for first aid and spill dilution is always compulsory.

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Adequately vented	Adequate location and separation	Detection and Alarm	Status	Comments
Yes	Yes	Yes	Preferred	Standard for new installation Danger limited if product remains in the storage
Yes	Yes	No	Acceptable	
Yes	No	Yes	Acceptable	
No	Yes	Yes	Acceptable	
No	No	Yes	Unacceptable	
Yes or No	No	No	Unacceptable	
No	Yes or No	No	Unacceptable	

3.1.2 Loss of containment

As with runaway decomposition, this event can be realised in many ways, all of whose prevention must be practised. Common examples are :

- overflow
- defective gaskets
- human error (e.g. valve alignment / flange tightening)
- mechanical failure e.g. hoses, connections
- pump seal failure
- pressure relief

Later chapters detail the prevention measures. However, standards for control and damage limitation are according to the following table, which is derived from an assessment of risk of damage to people and environment in the event of a significant loss of containment.

Clarification of adequate containment, location, separation and detection is given in chapters 4 and 5.

Adequate containment	Adequate location and separation	Detection and alarm	Status	Comments
Yes	Yes	Yes	Preferred	Standard for new installations
Yes	Yes	No	Acceptable	
Yes	No	Yes	Acceptable	Emergency response
No	Yes	Yes	Acceptable	
Yes	No	No	Unacceptable, except under special conditions	High integrity emergency procedure required and no nearby combustible inventory
No	No	Yes	Unacceptable except under special conditions	
No	Yes or No	No	Unacceptable	A partial containment is indispensable. The reliability of the detection/alarm and emergency plan has to be proved

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3.2 Prevention of incidents

The most important elements of incident prevention are as follows:

- The avoidance of all contamination.
- The dedication of equipment to HP and avoidance of cross contamination by high integrity isolation from other chemicals and utilities.
- All equipment and fittings to be constructed from materials which are specifically approved and prepared for HP use.
- Equipment design standards to provide a high degree of mechanical integrity.
- All equipment to be provided with appropriate vents.
- Avoidance of contact with incompatible materials.

3.3 Detection and reduction of effects

The first step to reduce the effects of an incident is generally to **detect** any deviation as soon as possible:

- measurement of the temperature of the storage, together with an alarm when it increases.
- level indication and/or high level alarm on the tank, liquid detection,
- regular inspection and control of the plant.

The following features will **reduce the effect** of an incident :

- Adequate venting of the storage tank and its accessories,
- Safety shower and eyebath in the vicinity,
- Use of personal protective equipments,
- Location on a concrete surface provided with a retention basin,
- Safety distances between the storage tank and adjacent buildings,
- Supply of water for dilution of any spillage,
- Pre-planning of emergency response, together with appropriate training and practise exercises.

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4. HYDROGEN PEROXIDE STORAGE TANK

Minimum requirements and recommendations concerning the design and the construction of HP storage tanks are presented in this chapter. The diagram (p.19) representing a storage tank installation of HP presents essential items of equipment and, in addition, some optional features. The minimum requirements shall be installed in new storage tank installations and shall be considered for the evaluation and upgrade of existing storage tanks. The choice of the optional features should be considered in each individual case taking into account the local conditions.

Only atmospheric tanks should be used for HP. The tank can be either horizontal or vertical. It is essential that the tanks are built only by firms which are able to meet the highly specific requirements for producing compatible high integrity tanks and fittings. All HP tanks shall be of a mechanical quality and condition appropriate for storing hazardous chemicals. In any case, the design of the storage tank installation should be done together with a HP producer.

4.1 Temperature control

Temperature is the best parameter for the detection and analysis of the evolution of the situation in case of decomposition of HP. For this reason, it is recommended to measure permanently this parameter, to set adequate alarm and to monitor the evolution of the temperature in case of detected deviation (detection and alarm in reference to the §3.1.1, runaway decomposition).

The homogeneity of the liquid phase cannot be guaranteed (principally in the case of heterogeneous decomposition). We have to recognise that the measured temperature will not necessarily be representative of the whole content of the tank. Therefore it may be necessary, according to the size of the vessel, to install more than one temperature gauge. In order to get an adequate detection system, the recommendation for the number of temperature gauges is :

- 1 if $V < 100 \text{ m}^3$,
- 2 if $100 \text{ m}^3 < V < 500 \text{ m}^3$,
- 3 if $500 \text{ m}^3 < V < 1.000 \text{ m}^3$,
- 4 if $V > 1.000 \text{ m}^3$.

Since the surface of the liquid should have the highest temperature, an alternative technology consists in measuring the surface temperature (through infrared for instance) ; the number of measurement cells can be reduced to one or two, even in the case of big storage tanks.

Alarm : the decomposition rate increases with the temperature, the alarm should therefore be set as low as possible, in accordance with the local conditions. The first alarm can be set 5°C above the maximum normal liquid temperature ; the emergency alarm a further 10°C higher (refer to §8). Alternatively, the variation of the temperature of the liquid can be considered for the evaluation of a decomposition situation with the recommended alarm value of +1°C/h. Those recommendations are consistent with the emergency response presented in §8.

Alarm switches and thermocouples must not be of the mercury type, and the fluid used in the thermocouple well should be compatible with HP (no oil).

4.2 Emergency relief vent

The storage tank **must have an unobstructed emergency vent (minimum requirement)** to provide relief in case of decomposition. The best way is to install a loose manhole cover assembly that opens freely at low overpressure. It is desirable that the manholes are fitted with a loose wire mesh cover of appropriate material of construction to prevent large objects such as inspection torches, safety helmets, pens or tools falling into the tank.

The sizing of this emergency vent requires information on the worst decomposition scenario to be taken into account. The following cases must be considered for the evaluation of the adequacy of the venting system (in reference to the §3.1.1, runaway decomposition) :

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- Case A : the contamination of the tank with strong decomposition catalyst, typically alkaline products (e.g. caustic soda) can't be excluded. The safety vent has to be as big as technically possible : total opening roof (e.g. weak welding seam).
- Case B : the above case is excluded but the contamination of the tank with other decomposition substances has to be considered. A totally empirical approach, based on the analysis of past incidents, leads to a value of

$$200 \text{ cm}^2 / \text{t H}_2\text{O}_2 \text{ 100\%}$$

This value, independent of the HP concentration, is commonly used for the design of the relief vent by the users of HP.

- Case C : the storage tanks are located in highly controlled areas, where the organisation and the design of the plant reduces considerably the probability and the severity of a contamination (storage plant dedicated to HP for instance). A theoretical approach can be developed in those defined cases by the definition of the worst contamination scenario, taking into consideration:
 - the concentration of the stored product,
 - the volume of the storage,
 - the decomposition kinetic, based on the evaluation of the acceleration of the decomposition induced by the contaminants by laboratory tests.

Examples of this approach are presented in appendix 4.

In all cases, the design of the emergency relief vent should be developed together with a HP producer.

In order to minimise the consequence of tank burst, it is recommended to ensure the rupture at the top of the tank at as low a pressure as possible. One option is to ensure the frangibility of the roof (weak welding seam). In case of severe overpressure not contained in spite of the relief vent (a two-phases flow through the venting area in case of intensive decomposition is a factor of uncertainty in the design of the vent), the roof would open and act as safety vent, preventing any explosion of the tank.

In the case of existing installations where these design rules could not be adapted, it is necessary during the risk analysis that extra emphasis is placed on detection measures and emergency procedures (e.g. flooding or dumping).

It must not be assumed that a vent designed with the above method is a guarantee of safety : it is a recommendation which is intended to be used in conjunction with other preventive and emergency measures and not instead of them.

4.3 Detection of a loss of containment

The HP is not corrosive towards those appropriate materials of construction described in this guideline. For this reason, the probability of a leakage resulting from a corrosion of fixed pipes and connections is very low : a visual and regular inspection of the plant should be sufficient. Plastic installation should be inspected with care because of the risk of embrittlement. An overflow of the tank is much more likely to create a severe loss of containment.

Level indicator / high level alarm :

To detect any overflow of the tank, a high alarm should be installed : this alarm can be simply a level switch. It may automatically interrupt the filling of the tank in order to prevent any overflow.

A level indicator with high and low alarm may be preferred as far as it enables the monitoring of the peroxide inventory. Standard technology of measurement can be used, e.g. DP cell, float, radar or ultrasonic sensors (as long as **all** the materials of construction adopted are compatible with HP).

If the risk of overflow can't be excluded, it must be ensured that it does not represent any risk for the personnel and the environment : the overflow pipe must be directed into a safe location (e.g. catch bund).

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Liquid detection :

In order to exclude any uncontrolled pollution of the environment with HP, liquid detection can in some cases be necessary to warn the operating personnel and to enable timely corrective actions (for instance in case of inadequate or small catch bund). Standard technology of liquid detection can be used (e.g. vibration limit switch).

4.4 Containment

The tank should be erected on a concrete surface. To avoid any contamination of the environment following a leakage, the storage area should be provided with a retention bund. The adequate capacity of this bund should be defined according to the local regulation ; it should at least contain 110 % of the capacity of the biggest tank (if several tanks are located on the same area).

4.5 Materials

The selection of materials of construction to be used in service with HP must be undertaken with care, otherwise decomposition problems will be encountered. A list of accepted materials of construction (including use limitations) is presented in detail in appendix 5. It must be assumed that any material not listed is incompatible with HP and shall not be used unless compatibility tests have been performed with the assistance of a HP Producer.

The following materials are commonly used for the storage of HP :

Stainless steel :

Fully austenitic stainless steel is commonly used. The preferred grades are 304L or 316L. The welding quality is important ; it should be done by inert gas shielded processes, in order to avoid impressing impurities into the metal. A special care is needed with the finishing and treatment of surfaces, including pickling and passivation (see appendix 6).

Aluminium and its alloys :

High purity grades of aluminium (99.5 %) and the alloy Al-Mg3 may be used, but the fabrication with those materials is more difficult than with stainless steel. For fabrication work, argon shielded arc welding methods are used with rods of parent metal, with care taken to avoid impressing impurities into the soft metal. The tank shall be passivated before use.

Plastic material :

Some plastic may be used for small tanks (preferably up to 30 m³) and for concentrations of HP up to 50% weight. They must be very carefully selected and maintained. The mutual compatibility of the plastic and HP must have been demonstrated and the safe lifespan established. High density polyethylene is preferred for the tank. Particular care should be taken when using such materials as they are liable to degrade with time and are easily damaged in case of collision. They shall not contain any pigments, mineral fillers or catalytic residues incompatible with HP. If exposed to sunlight, they should contain suitable level of antioxidants and compatible UV stabilisers (consult an HP producer).

4.6 Ancillaries

Breathing vent

A breathing vent **must** be installed in order to prevent any over- or under-pressure (minimum requirement). The design of this vent should take into consideration the risk of contamination of the tank with particles present in the air (if any). A suitable filter should be installed if necessary.

Emergency discharge (optional)

In the strategy of protection of the tank against overpressure, an approach can consist in emptying the tank into the retention bund. This emergency discharge should be sized to prevent a bursting of the tank (in relation to the size of the relief vent) and must be operable from a safe place.

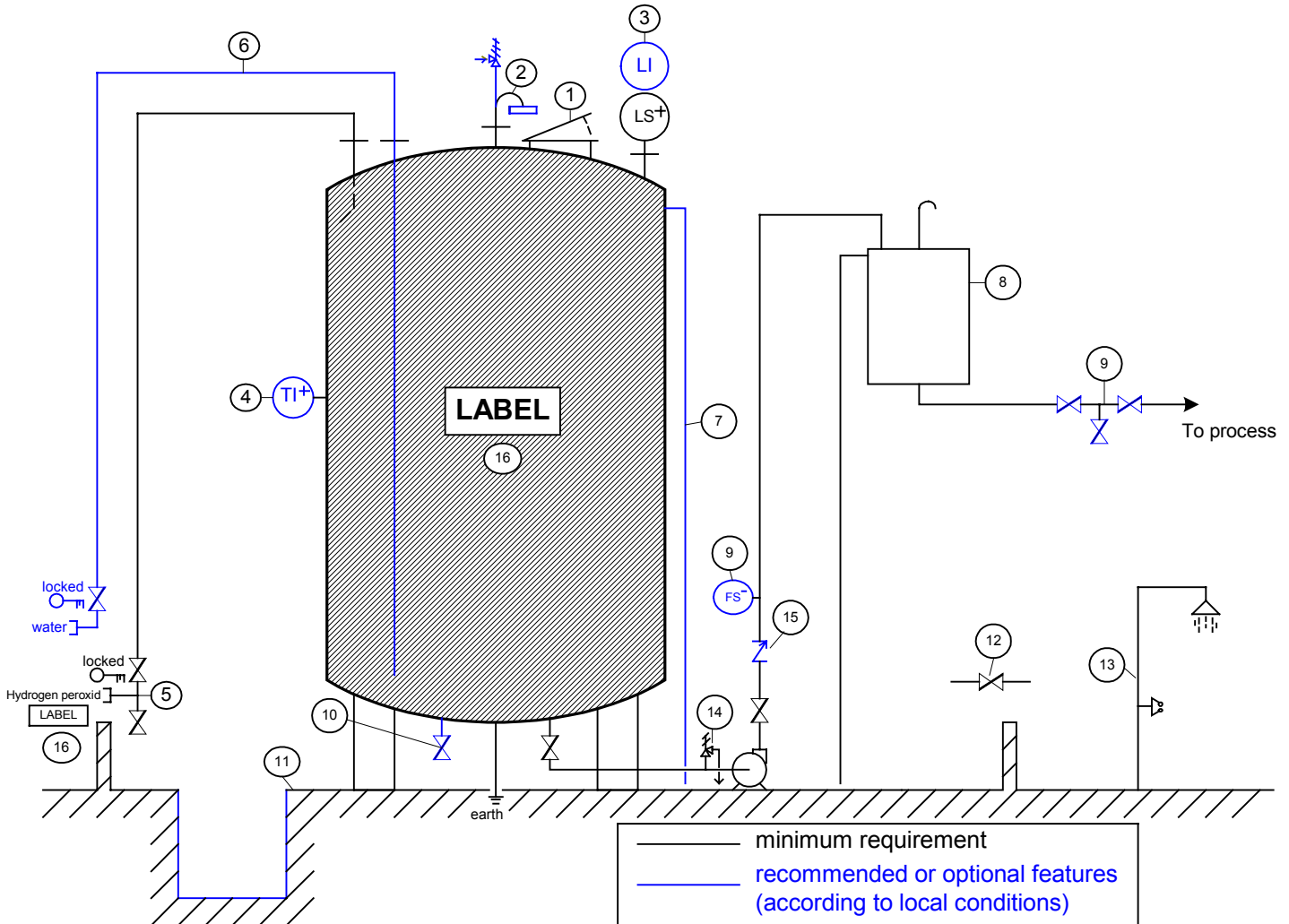
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Water source for cooling or flooding (optional)

A water source can be provided for safety reasons for cooling and flooding the tank in case of decomposition. The water flow-rate is dependent on the size of the tank and on the other protection devices (relief vent and emergency discharge). Deionised or potable water are preferred, but industrial water is acceptable. The water must be fed at the top of the tank, through a dip pipe (for mixing purpose). This pipe must in normal position be disconnected from the water feeding network (prevent contamination) ; the connection must be locked. It must be operated from a safe location.

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TYPICAL FEATURES FOR A HYDROGEN PEROXID STORAGE TANK



- ① Manhole - Emergency vent
- ② Vent (+ filter and vacuum relief valve)
- ③ Level alarm (+ level indicator)
- ④ Temperature indicator with alarm
- ⑤ Filling connection (with locked valve or cap*)
- ⑥ Water for flooding (with locked valve or cap*)
- ⑦ Overflow pipe
- ⑧ Intermediate tank (with overflow and adequate venting)
- ⑨ Low flow switch/ Block and bleed system (protection of the intermediate tank)
- ⑩ Emergency discharge/ drain valve
- ⑪ Bund
- ⑫ Water for spillage dilution
- ⑬ Safety shower and eye bath
- ⑭ Safety valve (for all possibly trapped section)
- ⑮ Check valve
- ⑯ Label (Tank, pipes and connection)

(*) cap with relief system or hole

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5. SAFETY DISTANCES

5.1 Location

Storage tanks should be preferably placed outdoors, away from heat sources and combustible materials. Tank location with respect to other tanks and equipment containing other chemicals must be considered carefully.

The tank and its accessories should be located preferably in a secured zone, only accessible to authorised personnel.

Piping and pumps should be located in readily accessible areas, but where they will not be easily damaged and where any leaking HP solution from a damaged line or flange will not fall on combustible materials or working areas.

Underground storage tanks should not be used. Indoors tanks or tanks on elevated floors are not recommended. In the case of indoors tanks, special attention during risk assessment should be considered. Aspects to be resolved are:

- vapour release, ventilation, evacuation and oxygen accumulation in case of decomposition.
- fire risks and drainage problems during loss of containment
- emergency relief venting to outside safe position
- emergency exits.

Tanks on elevated floors in existing installations are only acceptable if bunded and leakage control properly arranged.

When several HP tanks are in the same storage area or retention basin, their separation distances should enable to carry out all emergency actions and maintenance work to be performed correctly.

HP loading/unloading stations should be equipped with the adequate protection system to prevent mechanical damages of the storage tanks by transport vehicles. The loading/unloading station should preferably be isolated from other chemicals.

5.2 Safety distances

The determination of safety distances between atmospheric HP bulk storage tanks and objects for protection should proceed by risk evaluation and be judged in each individual case. As worst case scenarios, pressure burst of a tank and dispersion of HP droplets and vapour in decomposition situations should be considered.

This chapter aims to give all necessary information in order to proceed to the risk evaluation :

- **Fire** : as mentioned in the chapter 2, the hazard related to an external fire should only be considered in the case of small storage tanks. We recommend a distance of 7.5 meters between HP and combustible materials ³. This distance refers to the risk of fire of the combustible materials. A non-combustible wall may be located adjacent to storage tank as an alternative to the safety distance.
- **Pressure burst of a tank** : in case of inadequate venting, decomposition of HP could lead to a pressure burst of the tank. The overpressure wave generated by this burst may represent a risk for the personnel and the neighbour installation (domino effect). An example of calculation of this overpressure as a function of the distance to the tank is presented in appendix 3. Both chosen limits, 140 and 50 mbar, are considered in our approach as hazard limits for the equipment / buildings and for human beings. The calculation of the distances related to those overpressure values in each individual case should help to determine:
 - the risk to the neighbouring installation in case of pressure burst,
 - the safe distance for the personnel in case of decomposition.

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- **Emissions / dispersion in case of decomposition** : as mentioned in chapter 2, calculations of droplet behaviour suggest, that majority of the air-borne liquid would fall within a 20 – 30 meters radius from the vessel. In addition the dispersion behaviour of the HP cloud emitted through the safety vent also shows, that the IDLH value of 75 ppm is never reached at the ground level even though the cloud may drift in several kilometres from the source of release. If the decomposition occurs on the ground rather than in a vessel, then vapour dispersion distances could be extended further.

Gas and liquid phase explosion risk are not considered for the evaluation of the safety distance for the reasons mentioned in the chapter 2.

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6. AUXILIARY EQUIPMENTS

General guidelines to be observed in the design of auxiliary equipment:

- Always contact the HP producers in case of doubt about equipment described in this chapter.
- Use only approved **materials of construction** and suitable welding process as already specified in chapter 4. Consult the list of accepted materials in appendix 5; the compatibility of any material not listed shall be tested before use. Typical unacceptable materials are: graphite, brass, copper, nickel, bronze, chromium, iron and mild steel, synthetic rubbers.
- Take care that most **fluids (lubricants, hydraulic fluids, ...)** are incompatible with HP. Selected silicone or fluorocarbon based fluids are accepted (consult an HP supplier).
- All materials after manufacture or repair require **cleaning** and metals also require **pickling and passivation** by suitable formulation. See appendix 6.
- Avoid direct contact of **dissimilar metals** (especially aluminium and stainless steel).
- All pipeworks, pumps and equipment in which HP could be trapped must be always protected to **prevent overpressure** caused by HP decomposition.
- Avoid any accumulation of impurities (e.g. in dead ends or filters). The installation of filters should therefore be avoided. If a filter is required, consult a HP producer for the design and installation of the filter.
- **Label** clearly all lines and equipment and **dedicate** them exclusively to HP use.
- Ensure a **high standard of isolation** from other fluids (e.g. block and bleed connections).

6.1 Piping

All piping should be easily drainable; stagnant lines and dead ends should be avoided (against accumulation of impurities).

Pipework does not generally require insulation against freezing for the common commercial concentration (see physical properties of the HP solutions in chapter 1).

The design of the installation should limit the possibility of trapping any section containing HP. For this reason, the number of valves and fittings should be kept at a minimum. A **safety relief valve must be installed** wherever liquid trapping is possible.

Piping must be designed to prevent flow back by siphoning or any other means. A siphon breaker must be fitted if such an event is possible.

All open pipe connections must be protected from external contaminants by closing them when out of service.

Pipe connections:

Connections in piping systems should be butt-welded or flanged. Socket welded or screwed connections should be used only in special situations (i.e. instruments). The use of welded neck flanges is preferred. The flanges can be of raised faces or tongue and groove type. The connections must be free of oil and grease.

Lines under pressure should be equipped with flange protection guards when using raised face flanges in the case of a risk of projection.

Gasket : a list of accepted material for the gasket is given in appendix 5. Pure PTFE, PTFE enveloped or other types of PTFE without graphite or unknown additives are preferred.

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Safety relief valves:

The safety valve must allow the release of any gas generated as a result of the normal decomposition of non contaminated HP (standard commercial solutions). The generated flow of gas is low ; for this reason, the minimum commercial size of safety valve is sufficient. The case of the large diameter and/or long pipes must be studied individually. Pay attention to the compatibility of all the materials of construction of the safety valve (especially the multiple internal elements).

It is useful to standardise set pressures and dimensions for each installation.

The discharge of the safety valve should be directed into a safe location.

Valves:

The criteria for the choice of the valves (including check valves) are :

- no possibility of trapping HP in any position of the valve,
- compatible materials : this recommendation can be particularly difficult to observe because of the multiple elements in the valves : casing, shaft, gaskets, rings. Check all the elements of the valve in contact with the fluid.
- no need for lubricant.

Ball valves : a degassing hole must be drilled in the ball so that, while in the off position, the channel through the ball can be connected with the upstream liquid side. Those valves are commonly used for diameters below DN150. The hole diameter should be 3 mm minimum.

Globe valves : commonly used for all diameters.

Butterfly valves : used for diameters over DN150.

Diaphragm, plug and gate valves are **not** recommended.

Hoses:

Hoses should be minimised in number and length, dedicated and properly connected. It is preferred to reserve hoses for use only on a temporary basis (install fixed pipes whenever possible).

Choose carefully the type of hoses and their materials. In case of doubt, ask an HP producer (see material list in appendix 5).

6.2 Pumps

Centrifugal pumps are usually used for HP. Volumetric pumps are also acceptable. The use of other types of pumps should be discussed with an HP producer.

General recommendation: an emergency stop should be possible from a safe location (control room or local). Materials of construction should be selected according to the table in appendix 5.

Centrifugal pumps:

Shaft seal: single mechanical seal (recommended material: SiC/SiC. Alternatives : glass filled PTFE, alumina ceramic). O-ring: PTFE or perfluoroelastomers.

Avoid double mechanical seals (risk of HP trapping) and packed glands (risk of HP decomposition, incompatibility with lubricants).

Precautions should be taken to avoid pump operation against a dead end that may cause rapid temperature rise.

Volumetric pumps

Diaphragm, piston and gear pumps can be used. It is important to make a careful choice of materials of construction and intermediate fluid. The pump manufacturer should be informed about the risk associated with HP.

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Membranes should be in PTFE, stainless steel or zirconium. Only compatible materials of construction, even on the non-peroxide side, should be allowed in case of membrane rupture.

The piston should be a PTFE gland packing- plunger.

Protect volumetric pumps against overpressure generated by a closed discharge line. In case of installation of a safety valve, the discharge should preferably be connected to the suction side of the pump.

6.3 Intermediate tank

To prevent any back-flow, **a mechanical break upstream of the contact with any other product must be installed (minimum requirement)**.

An intermediate tank between the storage tank and the injection in the process is the best way to realise this break : do not rely on check valves or instrumentation (flow switch and isolation valve for instance).

This intermediate tank should have :

- a limited size,
- an overflow, to prevent any back-flow in the HP tank,
- adequate venting, preferably as big as technically possible,
- a temperature measurement (optional),
- a block and bleed system on the discharge line to the process.

The intermediate tank can also be used as a dosing tank for the HP.

6.4 Instrumentation

Users should seek advice from HP producers for the determination of the most appropriate type of instrument.

Take care that instruments do not involve trapping risks and that materials of construction are approved.

If conveying fluids are used in the measuring sensors, the fluid must be compatible to allow possible equipment failures.

Instrument air must be oil free and dry.

6.5 Safety facilities

Safety shower and eyebath must be installed in the vicinity. They must be tested periodically.

A **water source must** be available for a dilution of spills and leaks. All water supplies should be easily accessible, clearly labelled and available at all times with protection against freezing.

6.6 Unloading section (for users) :

HP must be preferably unloaded using a self-priming centrifugal pump ; this pump must be dedicated to the use of HP. The unloading by dry air (oil free) or nitrogen is nevertheless acceptable ; in this case, the gas system should be equipped with a proper filter, pressure reducing valve, safety valve and pressure gauge (do not use engine discharge).

In order to prevent contamination (unloading of another product), **a physical barrier must be established (minimum requirement)**, for instance by a cap or a valve closed with a key, under the responsibility of a responsible member of the personal of the plant.

Coupling : a dedicated coupling is recommended.

Pipes must be **dedicated** to HP : no cross connection, no common header.

Label clearly the unloading zone and pipes (particularly the connection point for unloading).

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Any spillage resulting from a disconnection of the hoses must not represent any danger : it can be recovered in the bund of the storage or be evacuated after dilution with a large quantity of water.

6.7 Dilution installation

Dilution of the product, - before, after or even during storage, is often practised because of the low concentration used in many applications, in order to reduce the transportation cost and/or the size of the storage tanks.

In case of a dilution before or during storage, use only demineralised or deionised water (typically, the requirement on the conductivity is lower than 1 µS/cm). It is not allowed to use steam condensate or boiler feed water. In case of a dilution after storage (or for direct use, without storage), the requirements on the quality of the water are not so high (respect the requirements of the process). It is recommended to perform stability tests to validate the quality of the water (those tests can be done by the supplier / producer).

The transfer line for demineralised water should be constructed with materials compatible with HP (this recommendation is mandatory for all sections of the line from where HP back flow can't be excluded). The design should ensure the impossibility to return HP into the water distribution network (don't rely on a check valve or on a simple isolation valve). The configuration of the pipe connections between HP and demineralised water lines should include an intermediate draining valve (block and bleed system).

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7. OPERATIONS

7.1 Supply

The unloading of bulk HP must be organised so that the following hazards are **specifically** avoided:

- Delivery of HP to any destination other than its intended dedicated tank or via any route other than its dedicated pipework and associated equipment.
- Delivery of any other substance to the HP tank or via the HP pipework and associated equipment.
- Contamination of the HP during the unloading procedure.
- Overfilling of the HP storage tank.
- Leakage or spillage of the HP, and resulting contact with people or environment.
- Overpressure and/or underpressure beyond the limits of equipment.

In order to achieve these objectives, the following features will normally be required:

- Validation of the product before unloading (check that it is indeed HP).
- Unloading will preferably be by means of a suitable dedicated pump (either on the vehicle or the recipients installation). Alternatively, air or nitrogen can be used provided that they are clean, dry, filtered, oil free, equipped with adequate overpressure protection and that lines are blown out prior to unloading.
- The unloading procedure includes provision for confirmed identification of unloading point, prestart-up check for correct valve alignment and absence of defects, dedicated capped hoses, full personal protective equipment(except breathing apparatus) for people involved, check of adequate ullage in receiving tank, and continued supervision during unloading.
- The responsibility for the unloading operation must rest with the installation management throughout. Unloading operations must be performed by trained personnel.

7.2 Dilution

Dilution of HP potentially has several adverse effects on its stability. In particular, the very act of dilution will reduce the concentration of stabilisers in the HP and so their effectiveness. In addition, even low levels of contaminants which are inevitably present in water can have the ability to cause serious destabilisation. Dilution will also cause the pH to increase.

The effects of any dilution operation on stability must be assessed in advance.

HP suppliers will normally offer advice or assistance if requested.

7.3 Handling

Handling operations should preferably be carried out in a dedicated, ventilated and clean area, free of combustible materials and heat sources. In accordance with normal industrial hygiene, activities such as smoking, eating and drinking should be prohibited.

Handling operations should be allied to approved methods and procedures, improvisation being forbidden. The following key principles should be embodied in operations:

- The need for care, especially in prevention of spills and contamination of the HP.
- Scrupulous cleanliness.
- Good housekeeping.
- Avoidance of all contact with incompatible materials.
- Equipment being kept closed to keep out contamination, while still permitting decomposition gases to escape.
- Equipment being restricted to what is specifically suitable, clean, passivated(where appropriate), and labelled as for HP only.
- Avoidance of any trapping of HP during a long period, even if the section in question is equipped with an overpressure protection.

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- Avoidance of use of inappropriate equipment by imposition of a rule to the effect that, whatever is not specifically approved, is forbidden.
- After use, portable equipment to be rinsed thoroughly with good quality water and drained.
- Decontamination by immediate drenching of anything which is contacted by HP.
- As a minimum, the requirement is for goggles and gloves for any operation. Increased levels of protective equipment where required for splashing or vapour exposure (see safety data sheet).
- No leather gloves.
- Avoid leather shoes where there is a risk of contact with HP.
- Proximity of and awareness of safety showers/adequate water supplies/eyewash bottle.
- Once removed, HP must not be returned to the tank .

7.4 Maintenance

All maintenance work on an HP installation should be controlled by a formal permit procedure which assesses the tasks to be undertaken, the current working conditions, and specifies appropriate safety precautions.

Because of the special engineering features required for materials of construction and fabrication techniques necessary for HP systems, great care has to be exercised in repair, modification, cleaning or other maintenance operation. In particular the person(s) undertaking the work must have the necessary competences to ensure that only suitable materials, correctly pre-treated and fitted, are used.

For the replacement of fittings gaskets or other accessories, it must be ensured that only like for like replacement occurs. Experience shows that even minor apparently inconsequential differences can result in serious safety problems e.g. minor grade changes in gasket materials, or subcomponent change in a measurement probe.

Storage installations should be routinely inspected for signs of leakage, damage, disrepair and proper functioning of components. In addition safety equipment must be regularly proof tested.

7.5 Disposal

All disposal operations must be carried out in compliance with all applicable regulations in such a way that the safety of people and environment is protected. The main options are as follows:

- HP can be flushed to sewer as long as it is diluted sufficiently to not present a hazard in the drains. It is recommended to keep the concentration of the diluted product below 5% for safety purpose. In addition HP can be destroyed on a waste water treatment plant (to avoid adversely affecting its operation, the HP concentration at the entry point of a biological treatment plant should be below 100 ppm).
- The HP can be prevented from entering the environment and disposed of as a dangerous waste. This may be done by absorption on a non combustible material e.g. sand, vermiculite, or by decomposition. In these cases particular care has to be taken with respect to the safety aspects.

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8. EMERGENCY RESPONSE

8.1 Emergency planning

In sites where there are HP tanks, it is imperative that an emergency response plan is available.

The emergency response plan, at least, shall provide directions for:

- actuation of an alarm signal,
- actions to be taken in case of dangerous situations with respect to HP, such as decomposition, fire, spillage.
- allocation of responsibilities,
- procedures for notification of responsible management and authorities,
- evacuation procedures (e.g. warning system, evacuation routes, registration and care of evacuees)

All personnel directly or indirectly involved in the storage and use of HP shall be familiar with the emergency response plan. The emergency response plan, where appropriate, shall also be discussed with and made available to the local authorities. This is especially important for the parts concerning off-site help (e.g. fire-brigade, hospital).

The emergency response plan shall be checked and updated in regular intervals. The effectiveness of the emergency procedures shall regularly be tested, ensuring that the people involved experience such an event once a year.

8.2 Runaway decomposition

There are two aspects of runaway decomposition, which must be taken into account. These are, the dynamics of its auto accelerating nature and the variety of its potential consequences. Firstly, its auto accelerating nature is such that in its early stages, it can occur very slowly, even imperceptibly. However as the decomposition progresses, it will go faster and faster, becoming hotter and hotter and eventually generating large volumes of gas and vapour in a very short period. Secondly, the rate of acceleration of a particular runaway decomposition event can be extremely variable, depending primarily on the nature of the causal contamination.

A particular decomposition emergency can develop over a period of e.g. few minutes or e.g. hours or even longer. At the point of discovery of a runaway decomposition, it is not at all obvious how much time may be available before the attainment of maximum rate of decomposition.

General ground rules :

The main principle to be applied is to ensure the safety of all personnel within range as the top priority. Actions to protect the environment or save product and/or equipment must be a secondary objective. Upon detection of a decomposition, the emergency procedure must adopt the following principle lines of action:

- **Removal of unnecessary/untrained personnel** from the zone of potential danger (criteria to be defined by discussion),
- **Communication** of state of emergency to other personnel and authorities as appropriate,
- If safe to do so, **intervention** by **trained** and **protected** personnel.

The intervention guidance is summarised below in the form of some important **general ground rules** followed by the available tactical choices:

1. It is essential to have a pre-planned emergency procedure.
2. All intervention actions must be with full protective clothing and by trained personnel.
3. In case of doubt or the unexpected, everybody should go to a safe location.
4. All HP out of containment (overflow, emission, dumped) should be diluted as much as possible in accordance with chapter 7.5.
5. Authorities must be notified in the event of environmental exposure.
6. Medical contact with specific HP treatment knowledge.

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Response options :

In the event of a decomposition emergency the choice of response usually depends on two main factors:

- Knowledge of the actual rate of decomposition,
- The size of the installation.

Knowledge of the **decomposition rate** may be conveniently classified as follows:

- A. Visible emission from vent or audible gas escape from vent or temperature increase above ~15°C above the normal liquid temperature. These are all signs of a decomposition, which may well be imminent and in all probability cannot be stopped (in case of conflicting evidence, audible and visual indicators should take precedence). The safe choices are evacuation and eventually remotely actuated emptying/dousing.
- B. Temperature increases less than ~15°C above ambient temperature. Subject to caveats about the reliability of temperature indication, this is an incipient decomposition for which intervention time may well be available (until type A indications develop). In this case, investigation, local dousing/emptying or spray cooling may be considered. For small tanks even stabiliser addition may be effective.
- C. Other knowledge e.g. known contamination, excessive bubbling of the liquid, indirect evidence such as unusual behaviour of process or equipment. In this case, all options are available until type B or A indications develop.

Comments:

Concerning tank size, in general, to increase the size of the tank will inhibit the effectiveness of the addition of stabilisers or any external cooling of the tank. However, there is no uniquely defined relationship or correlation. Stabiliser addition is unlikely to be effective unless an engineered means of mixing is incorporated. Spray cooling is unlikely to be effective except in the early stages of decomposition and then not for large tanks.

In the event of a large vapour emission, the emergency plan must address the safety of the people in a downwind location. They should either escape in a direction perpendicular to the wind direction, or be indoors with windows and doors closed and preferably upstairs at the downwind side of the building. Water curtains may be deployed by the fire brigade in case of decomposition at the ground level (e.g. decomposition in the bund after dumping of the product) in order to limit the dispersion of the HP vapours ; the risk of overpressure of the tank should be considered for the position of the fire brigade (in relation with the safety distances).

8.3 Loss of containment

In case of a loss of containment, the emergency response must consider the risks against the person and the environment, as well as the specific risk of fire, or even explosion in the event of contact with flammable materials if confined e.g. in drains, pits or closed collection tanks.

8.3.1 Fire fighting

HP will not burn, although it can initiate combustion of combustible materials and contribute to an increased ferocity of burning. The application of water is recommended for all fires involving HP. In the event of HP being exposed to an adjacent fire, water spray cooling of the HP equipment may be applied to prevent accelerated decomposition, but only if this can be achieved from a safe location. This recommendation applies mainly to small tanks ; for larger tanks, experience shows that it is unlikely that a surrounding fire would cause an hazardous increase of the temperature of the HP.

In all cases personnel protective equipment is required. If there is a risk of explosion, water application must be from behind protection.

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8.3.2 Environment

HP should not be discharged to water courses or soil. If necessary, spillages should be contained, by use of an inorganic absorbent such as sand or vermiculite, to prevent entry to the environment.

In case of discharge to the environment, the appropriate authorities should be notified without delay. Refer to chapter 7.5 for details.

UNDER NO CIRCUMSTANCES SHOULD HP BE DISPOSED OF BY TRANSFER TO ANY VESSEL. ESPECIALLY NOT USE ANY GENERAL PURPOSE WASTE TANKERS OR VACUUM TRUCKS.

8.3.3 First aid

HP is corrosive to the skin and mucous membranes and can cause severe damage to the eyes while direct contact. At any place where HP is stored or handled, appliances must be available for extensively washing skin and eyes.

Unless mentioned otherwise, in case of an accident any person may carry out the following actions, whether or not trained in first aid.

⇒ Skin exposure

- Rinse with copious amounts of cold water,
- If skin burns develop, rinse continuously with cold water for 15 minutes,
- Immediately remove contaminated clothes, avoid own skin contact (place clothes in water to prevent spontaneous ignition),
- Cover burnt skin with sterile gauze,
- Consult a doctor.

⇒ Eye exposure

- Immediately rinse with lukewarm, slowly running water, during which the eyes shall be kept open; this shall be maintained for at least 15 minutes,
- In case of serious eye injuries, continue irrigation during transport of the patient to an ophthalmologist,
- Immediately consult an ophthalmologist .

⇒ Swallowing

- Do not induce vomiting
- Rinse mouth and give plenty of water to drink only if the patient is conscious,
- Keep patient quiet and warm,
- Consult a doctor immediately.

⇒ Inhalation

- Remove the patient to fresh air and keep him quiet and warm.
- In case of symptoms of irritation of the respiratory tract and the lungs (coughing, shortness of breath), allow the patient to rest in a half upright position,
- Administer oxygen 8-10 litres per minute (trained personnel only!),
- Consult a doctor immediately.

In case of any doubt, refer to the safety data sheet (SDS).

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9. MANAGEMENT

The management shall appoint a sufficient number of well-instructed personnel to manage, to supervise and to handle the HP.

The management shall

- provide the technical means and facilities to store the HP in a correct and safe manner,
- provide accurate and unambiguous instructions for proper handling of HP,
- ensure adequate and sufficient maintenance, inspections and operating procedures,
- ensure emergency and fire-fighting plans.

The management shall audit the above mentioned elements regularly. Accidents or incidents shall be effectively investigated. Corrective actions must be implemented, their efficiency must be checked afterwards.

The management shall ensure that no modification of the installation and operating practises can be carried out without authorisation from competent responsible persons.

The management shall take care that the personnel involved in storage and handling shall be given adequate instruction and training, both in safe and proper handling of HP, and in emergency procedures to deal with spillage, contamination, decomposition, fires, ingestion, inhalation, skin and eye contact. Refreshment courses should be given at least once a year.

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Appendix 1

Decomposition kinetics of Hydrogen Peroxide

Reaction Kinetics



$$d[\text{H}_2\text{O}_2]/dt = -k [\text{H}_2\text{O}_2]$$

with : $k = 0.81 \cdot 10^7 \cdot k_F \cdot e^{(-10357/T)} \text{ min}^{-1}$
for uncontaminated product $k_F = 1$

Decomposition kinetics are accelerated by :

- Contaminants (Fe, NaOH, ...) : increase of k_F
- Increase of temperature
- Increase of Pressure (limitation of water vaporisation thus increase of temperature)

For contaminated product, see example of k_F values in the following tables (k values at 25 °C).

Experimental results with addition of Fe³⁺

Iron content (mg/kg)	$k \times 10^8$ min^{-1}	k_F	Comments
0.12	0.95	1.46	Standard technical grade 70% HP
0.37	3	4.6	
7.76	7.56	11.6	
15.52	9.42	14.4	
31.04	64.55	98.9	
38.81	912.5	1398	
46.6	6763	10366	
10	4476	6861	Unstabilized 70% HP
20	21760	33360	

Experimental results with addition of caustic soda in stabilised 70% HP

NaOH 100% (kg/m ³)	pH	$k \times 10^8$ min^{-1}	k_F
0	0.55	3	4.6
2	4.85	105	160
5.8	5	295	452
7	5.45	863	1322
12	5.8	2283	3499
17	6	35200	53950
26.4	6.2/6.45	70083	107415

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Case Study :

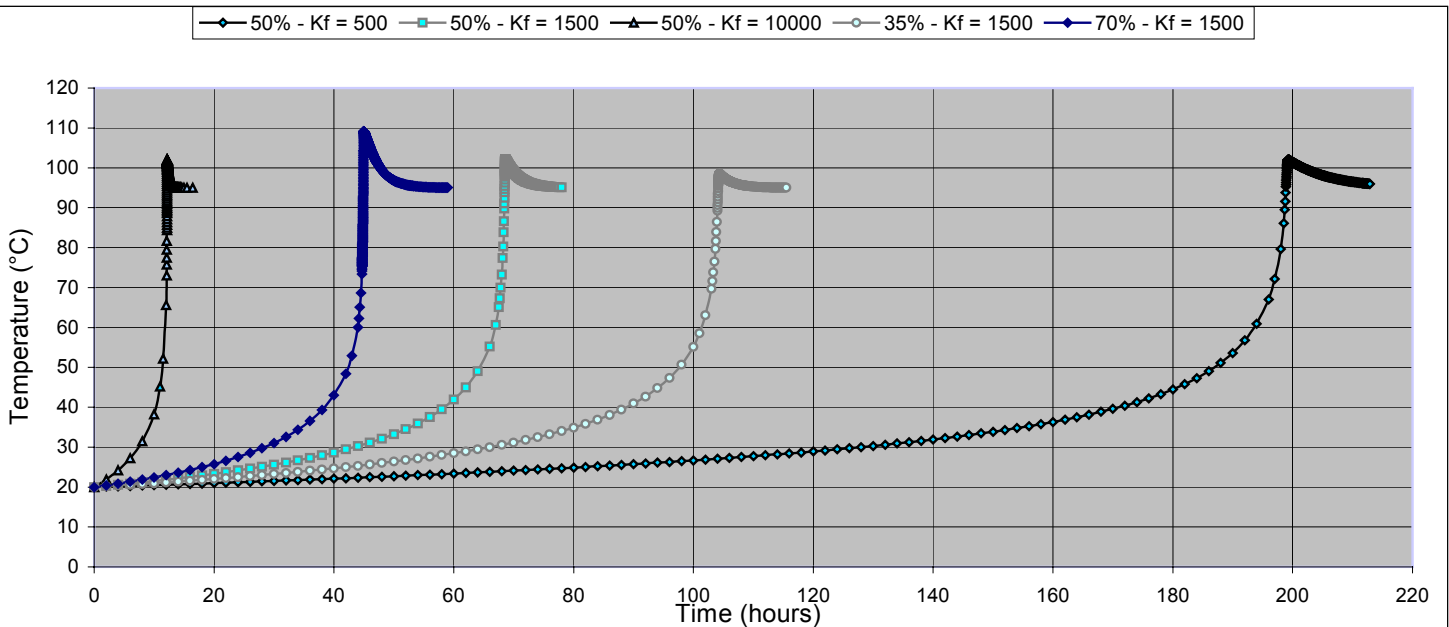
The following table and graph give, using a simplified thermodynamic model, an orientation concerning the variation of the temperature in the case of decomposition. The calculations are made under adiabatic conditions (which is conservative). The influence of the concentration and decomposition factor k_F on the decomposition kinetics can be seen through the 5 chosen examples:

- concentration 50%, $k_F = 500$
- concentration 50%, $k_F = 1500$
- concentration 50%, $k_F = 10000$
- concentration 35%, $k_F = 1500$
- concentration 70%, $k_F = 1500$

The following table indicates the temperature variation (in °C/h) at different temperatures, for the 5 above mentioned cases:

	50% - k_F 500	50% - k_F 1500	50% - k_F 10000	35% - k_F 1500	70% - k_F 1500
35 °C	0,3	0,7	3,5	0,5	1
45 °C	0,8	1,8	10	1,2	2,5
50 °C	1	2,6	15	2	5
60 °C	2,5	8	25	4	10
70 °C	5	35	90	10	23

The variation of temperature as a function of the time is represented on the following diagram. It shows that temperature alone is not sufficient to predict a runaway reaction of HP. The rate of temperature increase must also be taken into account.



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Appendix 2

Self Accelerating decomposition temperature

The Self Accelerating Decomposition Temperature (S.A.D.T.) is a very important parameter which is continually used in peroxygen technology. It is also often not fully understood.

HP and most peroxygen compounds are basically unstable, continuously decomposing with the evolution of heat. Material in a container will therefore progressively self-heat if the rate of heat loss to the surroundings is less than the rate of heat generation. As the temperature of the material increases, the decomposition rate and the rate of heat evolution increases. An accelerating reaction results. The S.A.D.T. of a system is the temperature of the surroundings above which a given quantity of material in a container of a given size and shape will generate an accelerating reaction. It is specific to that particular container and to that particular weight of the material. S.A.D.T.'s are, however, specified for many unstable substances in Product Descriptions and in Storage and Transport Regulations without any description of the container's size and shape, or of amount of its contents. These S.A.D.T.'s are derived from the standard maximum sized package and quantity of material which are used for products of that particular class. These conditions must be known before these standard S.A.D.T.'s can be used as anything more than a general guide to systems which involve different amounts of materials in containers of different size and shape.

In figure 1 the straight line AB shows the rate of heat loss from a container and its contents to the surroundings, as a function of temperature. The curved line CD shows the relationship between the material's temperature and its rate of heat evolution.

Points E and E1 are temperatures of the surroundings, and if the container and its contents are at these temperatures they will obviously lose no heat.

Point G is the point at which temperature of the container and its contents are in equilibrium with surroundings at temperature E.

If the temperature of the surroundings increases to E1 there is a new temperature loss line A1B1, which is tangential at point H to the heat evolution line CD. Container and contents will just remain in equilibrium with the surroundings when the temperature of the surroundings reach a temperature of E1. Any further increase in temperature of the surroundings and contents and container will progressively self-heat in an accelerating mode, irrespective of their initial temperature.

The surroundings temperature E1, is the S.A.D.T. of the system.

Point J is the Point of No Return. The temperature at point J is the Temperature of No Return (T.N.R.). Material above this temperature, put into a container in surroundings of temperature E, will self-heat in an accelerating mode.

At the S.A.D.T. the temperature of the Point of No Return coincides with the temperature at which the material and container are in equilibrium with its surroundings.

Deterioration of stability will move curve CD to the left, lowering the S.A.D.T. and vice versa. Increases of size and proportionally, contents in a series of containers of given geometry will reduce the slope of the straight line AB, giving progressively lower S.A.D.T.'s. Changes in geometry which decrease the surface/volume ratio will also reduce the slope of AB and the S.A.D.T.

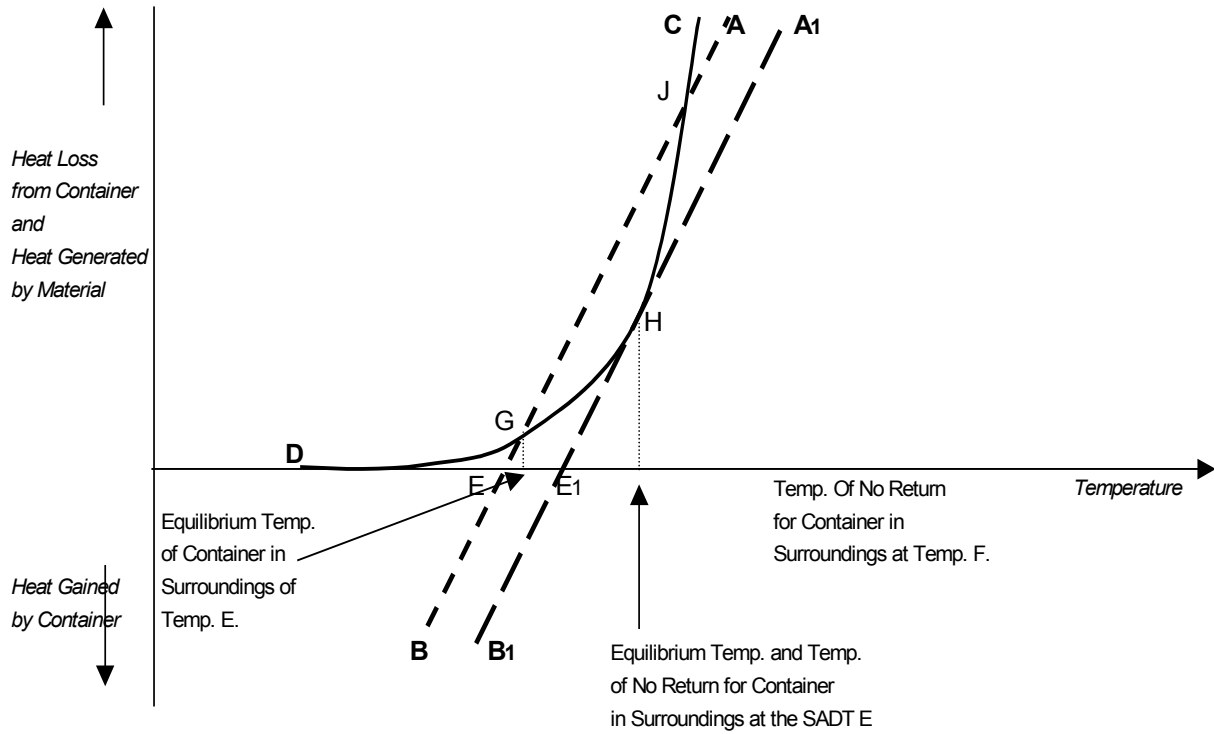
As HP is always decomposing and evolving heat, there will be a maximum size of storage tanks of a given geometry which can be filled with HP of a particular stability. As tanks increase in size, the amount of contamination which can be tolerated before the S.A.D.T is reached gets smaller and smaller. There will also be a maximum temperature for the HP which can be filled into a tank of given size and shape, in surroundings at a particular temperature.

In practical systems, considerations of S.A.D.T. do not have any great influence on the choice of storage tank sizes. Standard commercial grades of HP can be stored in tanks of over 1000 tonnes capacity in the hottest climates.

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S.A.D.T.'s and equilibrium temperatures of tank contents with the surroundings at the S.A.D.T., have been calculated and plotted in figure 2. For strengths of HP between 35 % and 70 %, the decomposition/heat rates change very little and a single rate equation can be used to give adequate accuracy. Very high strength materials do require modified rate equations. The S.A.D.T. and T.N. R. for a 17,5 tons I.S.O. tank full of 86% with $k_F = 1$ are 68°C and 80°C, compared with 81°C and 94°C for 35 % - 70 % material.

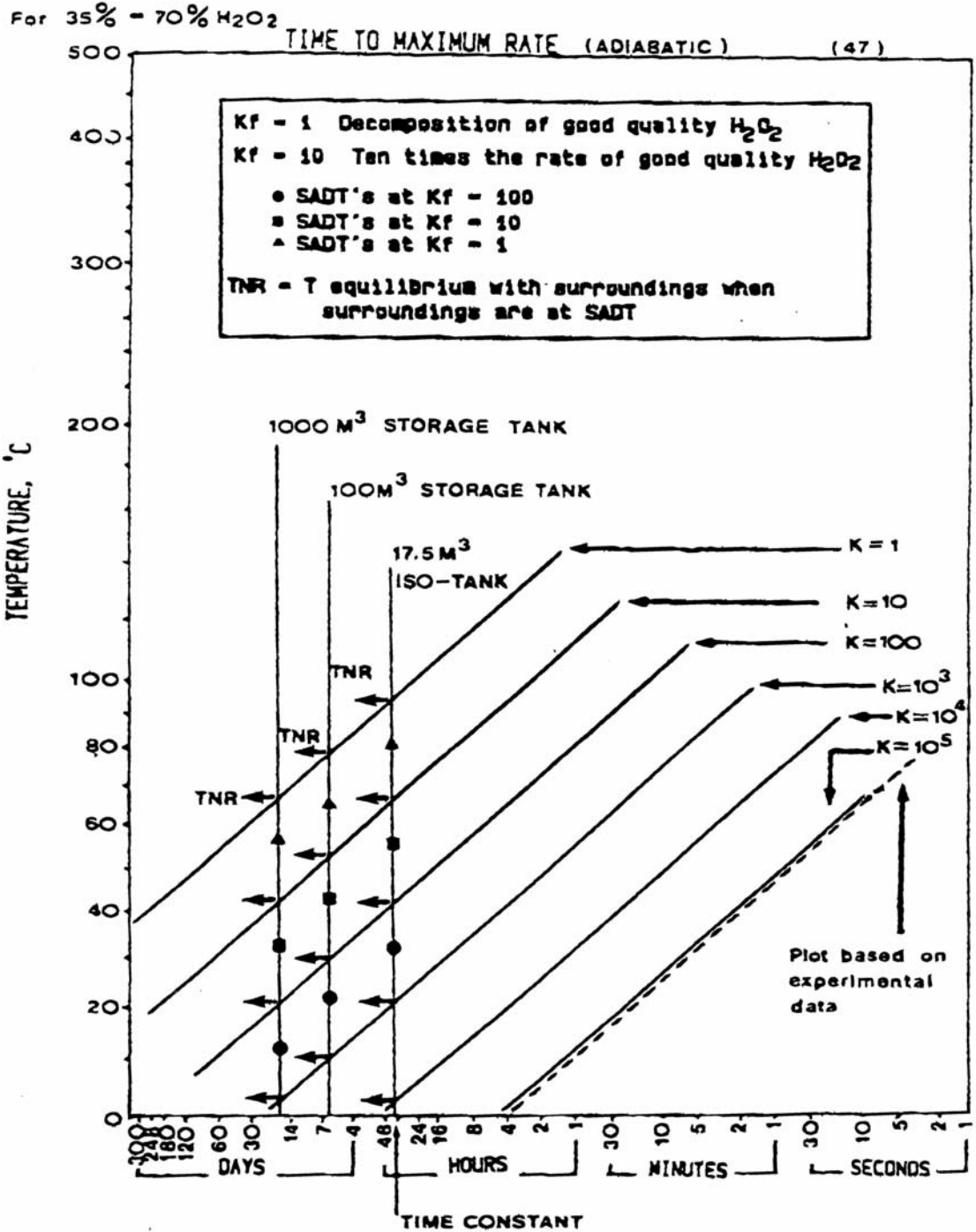
Figure 1 - TYPICAL S.A.D.T. DIAGRAM



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Figure 2 :

T.N.R.'S AND S.A.D.T.'S FOR TYPICAL 100m³ and 1000m³ TANKS AND 17.5 m³ I.S.O. TRANSPORT TANK



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Appendix 3

Example of calculation of the overpressure related to a burst of HP tank

using the TNT equivalence method

The following calculation method is only indicative. Other methods or criteria can be used to estimate the consequences of a tank burst.

We consider the following overpressure values as important for the determination of safety distances:

140 mbar : Lower limit for the major destruction of buildings. Considered also as a limit of lethality for people, not because of the effect of the overpressure on human beings, but because it corresponds to an empirical limit for the risk of projection of material.

50 mbar : Minor destruction of buildings (glass, light inner wall or weak structures). Limit for small injuries caused by glass breakage.

According to a chart, we can determine the “reduced distance” λ related to those both cases :

$$\lambda = R / \sqrt[3]{m}$$

R : distance to the centre of explosion

m : equivalent kg TNT

$\lambda = 10$ for 140 mbar

$\lambda = 25$ for 50mbar

For the calculation of **m**, we use the following calculation principle :

Energy released during the pressure burst (estimated by isenthalpic expansion energy of the gaseous phase) :

$$\Delta E = PV \cdot [1 - (P/P_a)^{(1-\gamma)/\gamma}] / (\gamma - 1) \text{ (in Joules)}$$

P : rupture pressure (Pa)

P_a : outside pressure (atmospheric - 1,013.10⁵ Pa)

V : gas phase volume of the tank (m³)

$\gamma = 1,4$ (ratio of specific heats)

50% of ΔE is considered to be utilised for the blast.

1kg TNT = 3,72MJ.

Caution : in the above calculation, the rupture pressure should not be confused with the design pressure. Rupture pressure of low pressure tank can be much higher than the design pressure.

With this calculation we can consider different explosion cases, in relation with the volume and the rupture pressure of the tank. Only the gas volume is taken into consideration for the calculation ; it is assumed that the tank is filled with 50% HP.

Total volume (m ³)	500	100	20	5
Volume V gas (m ³)	250	50	10	3
P rupture (bar g.)	0,2	1,0	1,0	1,0
ΔE (MJ)	3,8	4,4	0,9	0,3
m ~ TNT (kg)	0,51	0,6	0,1	0,04
R 140 mbar	8 m	8,4 m	5 m	3,4 m
R 50 mbar	20 m	21 m	12 m	8,5 m

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This calculation should be performed in each individual case for the determination of the effect of a pressure burst of the tank (if considered to be possible). The distances resulting from the calculation should be considered in the safety management of the plant (protection of the personnel and equipment).

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Appendix 4

Methodology for designing HP storage vents

This calculation approach⁴ can be used in the case of a foreseeable maximum contamination scenario. According to this approach, the required vent area can be obtained by the following relation:

$$A = f(c, p, k_F) \approx 0.35 (c / 100 - c) (k_F / \sqrt{p})$$

with

A	vent area	cm ² /t H ₂ O ₂ 100%
c	H ₂ O ₂ concentration	% weight
p	max. operating storage pressure	mbar g
k _F	H ₂ O ₂ decomposition rate factor (see appendix 1)	

c is known. p is the maximum allowed pressure ; it shall be less than or equal to the design pressure. The difficulty is to estimate the decomposition rate factor k_F.

This methodology takes into account :

- the storage volume and the HP concentration
- the storage max. operating pressure
- the HP quality
- the types and max. quantity of contaminants.

The both last parameters must be evaluated case by case and depend on :

- the connections with the storage
- the prevention equipment (dedicated coupling ...)
- the operators experience (producers/customers ...).

Calculation examples:

p = 50 mbar
k_F = 1.500

- c = 35 wt %	A = 40 cm ² /t H ₂ O ₂ 100%
- c = 50 wt %	A = 74 cm ² /t H ₂ O ₂ 100%
- c = 70 wt %	A = 173 cm ² /t H ₂ O ₂ 100%

Comparison with other calculation methods:

The results obtained with this k_F value are coherent with other usually used values, e.g. :

⇒ 200 cm²/t H₂O₂ 100% (recommended for small storage tanks)

⇒ Factory Mutual method : d = a * V^{0,493}

with

- d : diameter of the vent (cm)
- V : volume of the HP stored (m³)
- a : constant depending on the HP concentration (see following table)

HP concentration wt %	"a" values	Vent size cm ² /t H ₂ O ₂ 100%
35	4,77	⊃ 42
50	6,74	⊃ 56
70	15,8	⊃ 205

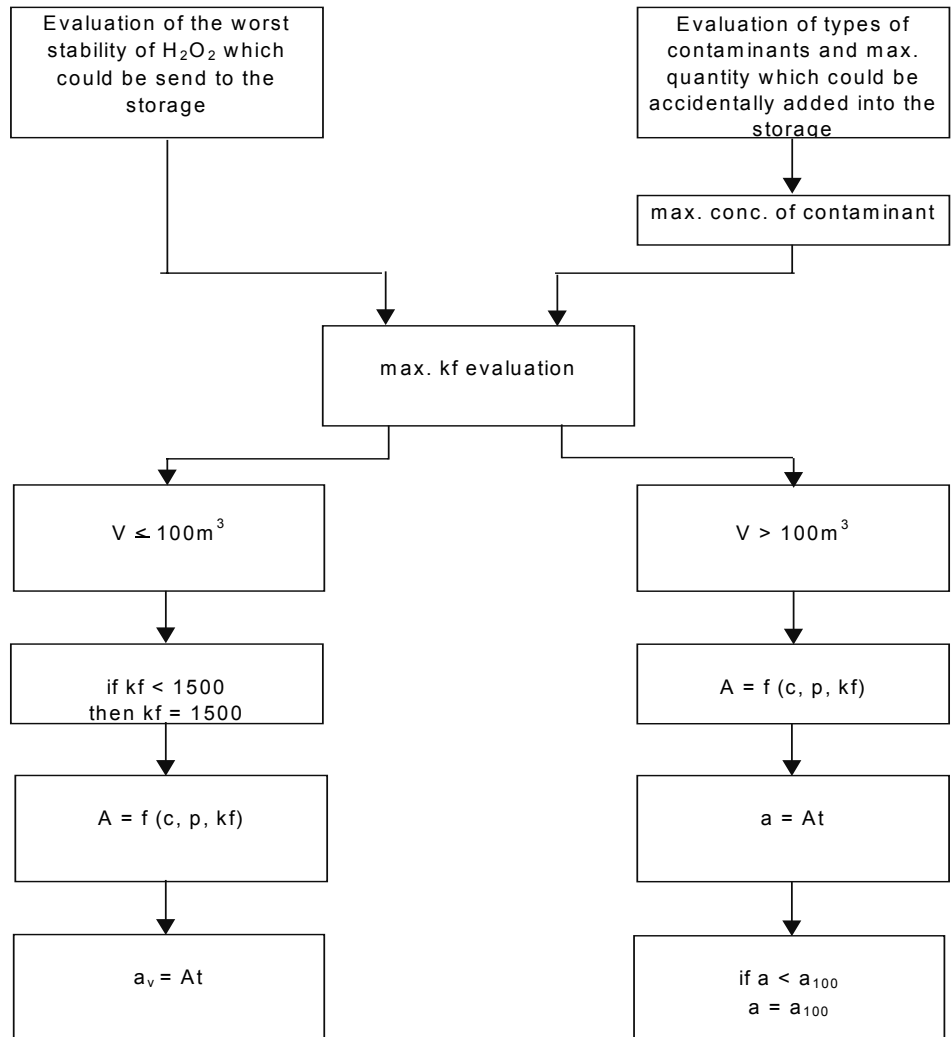
⁴ Protection of HP storage tank against overpressure – JC. Adrian, H. Lagarrigue - 1993

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Proposed methodology:

Risk analysis

Laboratory study complementary tests



t max. quantity of H₂O₂ 100% in storage
 a total vent area (cm²)

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Appendix 5

List of recommended materials

Part	Material	Class.	HP conc.	Comments
Storage tank	Stainless steel : 304L (1.4306) 316L (1.4404 – 1.4435) 316Ti (1.4571) 316 (1.4401)	1	Up to 70%	Needs pickling and passivation.
		1		
		1		
		2		
		2		
	Aluminium alloys : Al 99.5 (1060, 1080A) Al 5254, Al 5652 Al-Mg3	1	Up to 70%	Needs passivation. Pitting can occur in the presence of chloride ions.
		1		
		2		
	Plastics : HDPE	1	Up to 50%	For small tanks (up to 30 m ³). Susceptible to physical damage. Should not contain any pigments, mineral fillers or catalytic residues incompatible with HP. If exposed to sunlight, should contain suitable level of anti- oxydants and compatible UV stabilisers
		1		
Piping (pipe and fittings)	Stainless steel : 304L (1.4306) 316L (1.4404 – 1.4435) 316Ti (1.4571)	1	Up to 70%	See below
		1		
		1		
		1		
	Aluminium alloys : Al 99.5 (1060, 1080A) Al 5254, Al 5652	1	Up to 70%	See storage tank
		1		
		1		
	Plastics : HDPE PVC	1	Up to 50%	See below
		2		
		2		
PVDF PTFE	1	Up to 50%	Rigid, unplasticised. Inherently brittle, requires protection from impact and care in installation.	
	1			Up to 70%
Cast constructions (pumps, valves)	Stainless steel : 304 (1.4301) 316 (1.4401) 316Ti (1.4571)	2	Up to 70%	
		1		
		1		
		1		

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Part	Material	Class.	HP conc.	Comments
	Plastics : PTFE PVC HDPE PVDF	1 2 2 2	Up to 70% Up to 50% Up to 50% Up to 50%	See below
Gasket	Pure massive PTFE Expanded PTFE Glass loaded PTFE Perfluoroelastomer	1 1 1 2	Up to 70% Up to 70% Up to 70% Up to 50%	Pure massive PTFE is susceptible to creep ; suitable for tongue and groove flanges. For raised faces, prefer the others qualities of PTFE.
Hoses	Stainless steel : 304L (1.4306) 316L (1.4404 – 1.4435) (with outer SS braiding) Plastics : PE Reinforced PVC Reinforced Hypalon PTFE convoluted with outer SS braiding	1 2 2 2 1	Up to 70% Up to 70% Up to 50% Up to 50% Up to 70%	Excellent chemical resistance but prone to mechanical fatigue. Not recommended for big hoses (heavy and difficult to manipulate) Chlorosulfonated polyethylene
External bolts	Cadmium plated or stainless steel			Prevent rusting
Pipe thread sealant	PTFE tape			Ordinary lubricants should never be used
Thermowell	Stainless steel (316, 304)			Fluid : selected silicone based or fluorocarbon based

Classification : 1 : Material that are fully compatible with HP and suitable for a long term contact.

2 : Materials that are satisfactory for repeated short term contact with HP – performance dependent upon grade of material used.

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Appendix 6

Surface treatment of equipment in contact with Hydrogen Peroxide

The rules presented in this appendix shall be used for the treatment of all stainless steel or plastic equipment in contact with HP (tank, pipes, valves, accessories). Any equivalent surface treatment procedures may be used. For aluminium or other construction materials, the following procedure don't apply ; consult an HP producer.

1. Treatment of stainless steel

1.1 Scope and purpose :

This procedure shall apply to the surface treatment stainless steel mentioned in Appendix 5. Those steels cover themselves under the influence of atmospheric oxygen with an invisible passive layer that provides good corrosion resistance. Oxide films, hammer scales, annealing colours, and residues of weldslag – as produced in annealing, welding or fabrication – are not passive layers. These lower the chemical resistance of steel, just like embedded foreign matter, scratches or other mechanical damage and must therefore be removed. This has to be done using the following procedures. These procedures are very specialised and should be obtained from or validated by an HP producer. They assume that welds have been ground and polished as appropriate and verified by radiography during construction.

1.2 General :

The treatment procedure has to take place before the filling with HP. It must be ensured that no contamination occurs after treatment.

The following products are forbidden :

- chlorinated and halogenated solvents
- halogen ions (except for the pickling process)
- sodium and potassium hydroxides

Safety precaution the applicable codes and standards must be observed. The treatment fluids must be disposed of correctly in respect of the environment.

The composition of the treatment solutions (pickling and passivation) will be established by the surface treatment company and/or with assistance of an HP producer.

Water quality : water of drinking water quality with a maximum chloride content of 25 ppm is required for the preparation the solutions and for rinsing after pickling.

1.3 Global operation procedure :

Pre-treatment / Degreasing :

A mechanical process can be necessary to remove annealing colours and hammer scales. Brushing has to be performed with austenitic wire brushes. A simple brushing can be sufficient wherever no greater demands on corrosion resistance are made, for instance, for outside walls of apparatus and piping unless they are exposed to an aggressive atmosphere. Layer of hammer scale, adherent residues of slag, and embedded foreign matter cannot be completely removed by brushing.

Degreasing : this treatment will be executed by spraying or by complete dipping. The fluid is a solvent based on phosphoric acid or a detergent.

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Pickling :

The pickling process aims to remove by dissolution the surface layer of metal. The treatment process will be executed by spraying or by complete dipping, with pickling liquid or paste. The fluid is a fluoro-nitric solution. Solutions with a iron content higher than 8 g/l shall not be used. The pickling temperature must not exceed 50°C ; in general room temperature is sufficient. The maximum duration of the pickling process must be assessed in order to avoid a degradation a the metal surface.

Flushing :

It will be executed with demineralised water or drinking water if suitable at ambient temperature with hydro-pneumatic spray gun. The end of the flushing must be determined by the pH of the effluent being the same as the water source.

Passivation :

The passivation process aims to provide a protective oxide film on the metal surface. Passivation occurs naturally in contact with oxygen of air. For users installations, it is recommended to passivate using a nitric acid solution.

Final flushing :

Final flushing shall be carried out using demineralised water. The end of the flushing must be determined by the pH of the effluent being the same as the water source.

1.4 Inspection

Before filling the installation with high concentrated HP, it should be inspected and accepted by an HP producer. It is common to perform a test with diluted HP in order to verify the condition of the tank before the first delivery.

2. Treatment of Plastics

Visually inspect the internal surfaces of vessels and remove any adhering material.

Sweep out any loose debris.

Wash with a hot water (50°C) dilute aqueous solution of detergent. It is recommended that a 1 – 5 % solution of a good quality dodecyl benzene sulfonate based detergent is used. This washing may be achieved via spaying, scrubbing or swabbing.

Following washing, the equipment should be emptied and thoroughly flushed with demineralised water.

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