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RECOMMENDATION CONCERNING THE [redacted] LEVELS OF NITROGEN TRICHLORIDE IN LIQUID CHLORINE

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PREFACE

The production of chlorine has expanded rapidly in recent years and larger and larger quantities are stored, used and transported. The industry has a very good safety record, and any incidents which have occurred have in general led to consequences of relatively little importance. Nevertheless, the European chlorine producers, acting within the BITC, and wishing to improve further the general standards of safety have drawn up this recommended code.

The recommendations proposed in this code are based on the various measures taken by member companies of the BITC. They constitute a base line above which one is free to choose. They in no way are intended as a substitute f r the relevant national or international regulations, which should be respected in an integral manner. They result from the understanding and experience of the chlorine producers in their respective countries at the date of issue of this particular document. Established in good faith, they should not be used as a comprehensive working document, but as a guide which should, in each particular case, be adapted and utilised in consultation with a chlorine producer. Any potential user, therefore, should address their enquiries to a chlorine manufacturer before undertaking detailed implementation of the guidelines laid down in this code. This text may be modified in the future to take into account evolution of the technology and general technical progress.

This edition of the document has been drawn up by a Working Group "Storage Transport and Safety", to whom all suggestions concerning possible modifications should be addressed through the offices of the BIT Chlorine.

INDEX

RECOMMENDATION CONCERNING THE MAXIMUM LEVELS OF NITROGEN TRICHLORIDE IN LIQUID CHLORINE

1 OBJECTIVES OF THE RECOMMENDATION

All systems for holding liquid chlorine are designed to contain the maximum possible pressure which can be generated from the liquid or gas phase of the system. This pressure will, in general, arise from the vapour pressure of chlorine or from the gas pressure of an inert gas additive. However, two other circumstances need to be taken into account, the possibility of reactive conditions which could lead to generation of additional pressure in the gas phase and the possibility of reactive decomposition of impurities within the liquid. The former is avoided by careful control of the link between the chlorine system and other reactive materials (H_2, hydrocarbons etc). The purpose of this recommendation is to highlight the potential problems with accumulation of the reactive material nitrogen trichloride (NCl_3) in liquid chlorine and to describe the constraints which need to be observed in order to avoid the risks associated with its presence in routine chlorine storage, transport and use.

Any chlorine user who is uncertain of the potential problems which can arise from accumulation of NCl_3 in a system should consult the chlorine supplier to confirm that there is no exposure to an unacceptable or uncertain level of risk.

2 AREAS OF POTENTIAL CONCERN

2.1 Chlorine Liquifier

Most of the NCl_3 present in the chlorine gas phase will be condensed in a chlorine liquefaction process. Where only partial liquefaction takes places some concentration in the liquid will therefore occur.

2.2 Chlorine Storage

The operation of chlorine storage tanks can involve slow vaporisation of chlorine and concentration of impurities. NCl_3 has a higher boiling point than chlorine and any NCl_3 present in the gas will concentrate in the liquid phase. This could be a cause for concern in a storage system which is pressure controlled by recycle of gas, or in the venting down of storage containers prior to emptying.

2.3 Mobile Containers

The use of these containers becomes a cause for concern when chlorine is withdrawn from the gas phase, rather than by direct discharge as liquid to storage, vaporisation or other process use. Whenever the chlorine supplier or user cannot be certain that the chlorine will be removed as liquid, then suitable precautions must be taken to ensure that the chlorine has a low NCl_3 content (ref 3.3), or that the residual liquid is not allowed to develop a high concentration of NCl_3, or that the contain r/system does not collect the residues in a confined volume.

DO 072929
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2.4 Vaporisers

Chl rine vaporisers, particularly constant volume vaporisers such as kettles, are equipment where high boiling impurities

are likely to collect. Careful checks must therefore be maintained on the quality of the chlorine fed to such equipment, and of the concentration of impurities in the residual liquid. Where the equipment or process is such that dangerous concentrations could occur, material must be drawn off periodically to a purge vaporiser.

In the case of a constant volume vaporiser it may be preferable to operate the purge system continuously to prevent an NCl_3 build-up and to facilitate subsequent venting down.

Some chlorine gas treatment processes make use of a direct contact pre-cooler and reboiler system where higher concentrations of NCl_3 can collect. Where the system operates at low temperatures, care must be taken to avoid a dangerous concentration being reached. Systems operating at higher temperatures need to be controlled, but in general it can be demonstrated that NCl_3 collects in the liquid and is then decomposed at temperatures of 50-70°C. Another safeguard is to use a system where liquid is run off, diluted with carbon tetrachloride and then maintained at temperatures of ca 50-70°C to decompose the NCl_3.

2.5 Other Situations

Periods of upset conditions, or preparation for maintenance, can lead to an increase in levels of NCl_3. For example emptying of a container by venting down prior to maintenance, the passage of liquid into a heated catchpot on a chlorine relief system etc, could be a potential hazard and should be taken into account in plant design and operating and maintenance procedures.

3 LIMITING LEVELS OF NCl_3 IN CHLORINE

3.1 Basic Principles

On the basis of the experimental results indicated in Appendix 1, it is calculated that, on detonation, a mass of 1.5 gms of pure NCl_3/cm^2 of metallic surface wetted is capable of fracturing the metal of a typical chlorine vessel. Appropriate safety measures therefore, should have as their objective that this critical mass loading should never be reached, during either normal or abnormal operation, of the chlorine containing system. The experimental results show that a concentration of NCl_3 in solution greater than 3% w/w at ambient temperature is capable of an accelerated decomposition which is strongly exothermic. This concentration should also nev r be reached at any time.

3.2 Maximum Level Inside Any Equipment

The maximum admissible concentration of NCl_3 at each point in a liquid chlorine installation (production, storage, transport or use) sh uld be limited in a way which always r spects the basic principles enumerated in 3.1. Consideration sh uld be given to:

- the inherent risk of exceeding any safety margin
- the variation of measured NCl_3 c ntents with time, and any imprecision introduced by th meth d of sampling and analysis
- the peri d f time betw en successive measurements

A supplementary safety margin should be incorporated into the prescribed levels of NCl_3 for different situations. It is therefore recommended that in order to avoid reaching a level of 3%, the NCl_3 concentration should be limited to 1% in all parts of the installation where NCl_3 could concentrate during normal operation. Where frequent checks are not carried out, this limit should be reduced to 0.1% or 1000 ppm. This limit of 1000 ppm should be maintained for all reboilers and vaporisers, and in the residues obtained when emptying stock tanks.

3.3 Maximum Levels of NCl_3 Introduced Into Fixed and Mobile Tanks

The allowed NCl_3 levels have been established taking into account the potential concentration of NCl_3, particularly where there is intended or accidental vaporisation of the chlorine in the gas phase. All calculations carried out for a specific installation, should take into account:

- the quantity of NCl_3 which might be present after complete vaporisation of the chlorine
- the dimensions and the overall geometry of the container

The calculated maximum levels of NCl_3 in liquid chlorine introduced into vessels of various dimensions, where the chlorine could be removed in its entirety as gas, ignoring the effect of any diluents, and where the quantity of NCl_3/cm^2 of residual surface wetted remains below 0.3 gm/cm^3 (see Appendix I) is as shown in the following table for containers of various sizes. In order to provide a large factor of safety a second set of figures is provided to indicate the recommended level of NCl_3. For all large storage containers, chlorine should only be removed as liquid, but a limiting NCl_3 concentration is recommended to provide a safety margin to cover all possible circumstances of removal of chlorine as vapour.

Vessel Capacity	Maximum Concentration of NCl_3 (ppm w/w) in Liquid Chlorine	
	Calculated	Recommended*
50 kg	200-300	20
1000 kg	50-60	20
20 t	15	5
50 t	8	2
>300 t	5-6	2

*20 ppm w/w NCl_3 is the generally accepted maximum level for liquid chlorine for all BITC liquid chlorine manufacturers.

The recommended values for each type of container are as indicated below.

DO 072931
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3.3.1 Chlorine Storage

Particular attention is required to cover the following circumstances.

In the case of low pressure storage (reference GEST 73/17), there is a progressive loss of contents by vaporisation. Greater care therefore must be taken to ensure that the NCl_3 remains at a low and predictable level. This becomes most important when the container is nearly

empty, particularly prior to being taken out of commission. Prior to commencing the emptying operation, it is wise to set an upper limit of 5 ppm NCl_3 in the liquid chlorine present in the vessel, and to introduce a quality of liquid necessary to achieve this figure. If any container and associated pipework has low points (sump, branches etc) where liquid chlorine could collect, and which is not readily removed during the emptying operation, the system should be flushed with liquid containing <2 ppm NCl_3 before the final contents are run down.

Appropriate precautions should be taken with normal pressure storage tanks if they are emptied by vaporisation of the final contents. In all normal situations for pressure storage applications with liquid discharge the recommended maximum level for liquid chlorine introduced is 20 ppm NCl_3.

3.3.2 Small Mobile Containers

Chlorine cylinders or drums of up to one ton are frequently used for extraction of chlorine as gas rather than liquid. Their size however, is such that dangerous quantities of NCl_3 rich material will not accummulate at the later stages of emptying if a limit of 20 ppm NCl_3 is set for chlorine put into small containers.

3.3.3 Bulk Transport Containers

Almost all road tankers of liquid chlorine deliver directly to customer storage and it is only in well defined circumstances that gas is supplied to a point of use. Most rail tanks are also used in prescribed deliveries to customer storage where the mode of operation is guaranteed to be the direct discharge of liquid. The NCl_3 limits therefore, are set by the use to which the chlorine will be put or by the behaviour of the residual chlorine left in th vehicle until refilled. The recommended limit for NCl_3 in these circumstances is 10 ppm, possibly 20 ppm for smaller containers or for chlorine known to contain significant amounts of bromine or other diluents.

On the other hand iso-containers and certain tank deliveries may be used for chlorine gas discharge to a process. In these circumstances, or in any other cases of uncertainty, the NCl_3 limit should be set at 5 ppm to avoid any problems with the residual material. Such containers should preferably not be fitted with a sump or any other configuration of equipment where a small heel of liquid can collect, unless the maximum level of NCl_3 limit is reduced to below 2 ppm.

4 SAFETY MEASURES

4.1 Principles

The most important control over the potential levels of NCl_3 is at source in the chlorine producing process.

Whenever the chlorine producing process or source of raw materials are changed, a check should be made to ensure that a new NCl_3 risk has not been introduced (change of anode type, water, settling aids, salt source, drying acid). For electrolysis units, a regular check should be maintained on the total nitrogen compounds in the brine. Any modification to the materials used in the process should always be accompanied by a check against any potential problems connected with NCl_3

4.2 Frequency of Testing for NCl_3 in Liquid Chlorine

The appropriate frequency of testing should be determined by experience and by the extent of variation in the results obtained. As an indication, however, the following frequencies are set as a guide.

4.2.1 Whenever the NCl_3 level is capable of varying between 0.1 and 1%, an analytical check should be carried out each week, in particular on the purge line from vaporisers or condensors.

4.2.2 Whenever the NCl_3 content is normally >100 ppm (0.01%) and less than 1000 ppm (0.1%) the analytical checks should be carried out at least once/month. This frequency is also appropriate for chlorine from a liquefaction system where the NCl_3 lies between 20 and 100 ppm.

4.2.3 For chlorine systems where the NCl_3 level is typically 5-20 ppm the analytical frequency should be once/3 months on liquefaction output and on randomly chosen storage/mobile containers. In other liquid systems where the level is < 5 ppm the frequency of testing is satisfactory at once/year.

During periods of commissioning, maintenance, process modification etc, whenever there is a risk of higher NCl_3 levels, the above frequencies should be increased. Regular checks, at an appropriate frequency, should be maintained on the output from any NCl_3 destruction system, eg U/V irradiation of gaseous chlorine.

4.3 Temperature Limits

Purge vaporisers are used industrially to destroy NCl_3 and temperature limits are set to achieve a controlled decomposition rate, while at the same time ensuring that local overheating of metal surfaces is avoided.

Because of the influence that increasing temperature has on the relative explosive decomposition rates of NCl_3, care should be taken to control the temperature of equipment handling liquid chlorine containing high levels of NCl_3 (0.1-1%). Overheating of the chlorine should be avoided and therefore direct electrical heating systems should not be used. A purge vaporiser can be designed to operate with low pressure steam at 120°C to facilitate slow decomposition of NCl_3. Otherwise, one should employ a heat transfer fluid, for which the temperature can be limited to 80-90°C, thereby ensuring that the liquid chlorine containing NCl_3 does not exceed 80°C.

4.4 Construction Details for Vaporisers and Reboilers

All equipment where there is a risk of NCl_3 accumulating, as a result of the progressive vaporisation of liquid chlorine, should be fitted with a purge point at the low point of the system, to enable the residues to be purged in any instance where there is an excessive increase in NCl_3 levels. It is als possible to treat these residues by dilution in carb n tetrachloride before thermal decomposition. Such diluti n permits the system to remain always at a NCl_3 concentration of less than 1%, ven aft r vaporisati n of the chlorine.

5 ANALYSIS OF NITROGEN TRICHLORIDE

The analysis of NCl_3 in liquid chlorine requires specialist analytical equipment as described in the BITC publication*. The analysis of low concentrations is the most difficult and care must be taken to avoid contamination of the samples with other nitrogen compounds.

REFERENCES

*Analytical method - BITC Analytical Procedure. "The Determination of Nitrogen Trichloride in Liquid Chlorine" 20 May 1981.

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APPENDICES

1 PHYSICAL AND CHEMICAL PROPERTIES OF NITROGEN TRICHLORIDE

Nitrogen trichloride is formed during the electrolytic production of chlorine, due to side reactions between the chlorine and various nitrogen compounds in the brine solution. It is a liquid with a boiling point of 71°C, which is miscible in all proportions with liquid chlorine and other chlorine compounds such as carbon tetrachloride.

Nitrogen trichloride can also decompose exothermically, and in the concentrated form the liquid behaves as a sensitive explosive, capable of rapid deflagration and detonation. The explosive nature of the material when mixed with liquid chlorine (and similar materials) is very dependent on both its concentration and on the total amount present. Pure liquid NCl_3 has been calculated to be capable of generating a detonation pressure of 5.5 to 7.5 x 10^3 atm. At very high concentrations in liquid chlorine it could generate an energy release equivalent to 30-40% of the explosive force of TNT. Concentrations >35% by weight are readily capable of detonation by shock, high temperatures or ultra-violet light, 13% NCl_3 appears to be the limiting concentration to achieve detonation. Even at low concentrations, NCl_3 will slowly decompose, the decomposition increasing with the temperature, or in the presence of metals such as copper or alloys like monel. Ultra violet light can be used to decompose NCl_3 safely, when it exists as a minor component in the gas phase.

As the concern over the explosive behaviour of NCl_3 is in the context of mixtures with liquid chlorine, the important factor is its explosive force when contained within a typical chlorine pressure vessel - with a wall thickness of say 10-12 mm. The available evidence from the published literature indicates that detonation of 1.5 g NCl_3 (as 100%)/cm^2, within a liquid film would be capable of fracturing the metal, and 0.3 g/cm^2 of surface area is capable of overstressing the metal to the point of cracking or fissurisation. The calculation of the potential explosive capability of an NCl_3/Cl_2 mixture within a vessel is only an approximation. As the chlorine evaporates the concentration of NCl_3 will progressively increase, but if the residual pool covers a large area, or the NCl_3 concentration is still <13%, the explosive potential remains small. On the other hand if the residual liquid collects in a sump or bottom drain connection, the critical mass may be reached sufficient to cause total metal failure. Experimental work has also shown that chemical decomposition of NCl_3 in liquid chlorine at >3% is rapid and strongly exothermic.[3]

The above summarises the properties of NCl_3 in the presence of the much more volatile liquid chlorine.[3] In the presence of high r boiling impurities which act as inert diluents and which are also found in commercial chlorine, such as br mine and C_1 r C_2 chlorinat d carbon compounds, the hazards from NCl_3 accumulating in the residues from evaporation are reduced by dilution. On the ther hand, if it is possible in certain processes to f rm th r reactive materials in liquid chlorine, in these circumstances the expl siv energy f the mixture would be incr ased.

2. SOURCES AND DECOMPOSITION OF NITROGEN TRICHLORIDE

2.1 Sources of its Formation

NCl_3 could be formed from the introduction of nitrogen compounds into various parts of the brine or chlorine handling systems. Nitrogen compounds in the brine used for aqueous electrolysis are the main source of NCl_3 and only 1 ppm of NH_3 in brine is needed to give >50 ppm NCl_3 in liquid Cl_2. Rock salt, or in particular solution mined salt using surface waters, will contain varying levels of ammonium and nitrate salts, whereas the use of vacuum salt in the brine recycle circuit will give very low levels of NCl_3, except where ferrocyanides are added to avoid caking. [3] Chlorination or hypochlorite treatment of the brine is however, capable of destroying a large proportion of the ammonium salt impurity. NCl_3 can also be formed from other nitrogen based impurities in the electrolytic cell and for example the proportion of NCl_3 impurity could change due to a change in process conditions such as conversion from graphite to metal anodes. In plants which use direct contact water cooling of the chlorine gas before drying and compression, it is also possible to form NCl_3.

2.2 Destruction of Nitrogen Trichloride

Certain chlorine handling and liquefaction systems are capable of removing NCl_3 from the chlorine stream. Various processes which can be used to reduce the hydrogen content of cell gas - eg ultra violet light or active carbon can also preferentially decompose NCl_3. High metal temperatures, particularly of copper based alloys at temperatures of 80-100°C, will also decompose the material. Liquid chlorine and mixtures of chlorine with carbon tetrachloride maintained at 50-70°C leads to a progressive destruction of NCl_3. Alternatively, NCl_3 can be eliminated by reaction in a number of chemical processes, eg absorption of chlorine containing NCl_3 in caustic soda.