

## Safe handling of chlorine from drums and cylinders (second edition)



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This booklet gives guidance on the safe use of chlorine from drums and cylinders.

It is aimed at employers and employees in a range of industries which use chlorine containers. It will also be useful to safety professionals. © Crown copyright 1999

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This guidance is issued by the Health and Safety Executive. Following the guidance is not compulsory and you are free to take other action. But if you do follow the guidance you will normally be doing enough to comply with the law. Health and safety inspectors seek to secure compliance with the law and may refer to this guidance as illustrating good practice.

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## **Preface**

The aim of this guidance is to help those responsible for the safe use of chlorine from drums and cylinders to meet their obligations under health and safety law.

The guidance, like the document that preceded it, was prepared by the Health and Safety Executive (HSE) with help from the UK chlorine producers, users, trade unions, the Water Services Association, and the Chemical Industries Association (CIA).

We are grateful to all those who contributed and to Wallace and Tiernan for permission to produce the diagrams on pages 11 and 12 and to North West Water for permission to take the photographs shown in the text.

Where reference to British, European and other standards is made in this document, equivalent standards are equally acceptable alternatives.

You may need help beyond that given in this guidance. If you do, your chlorine supplier, and trade and employer associations such as the Chemical Industries Association or Euro Chlor, offer a range of advice and support. These and other sources of information are given in Appendix 4.

## Introduction

1 This guidance deals with the control measures for the safe storage and use of chlorine in cylinders (ie receptacles of 33 kg to 73 kg capacity) and drums (ie receptacles of about 870 kg to 1 tonne capacity). It does not deal with the bulk handling of chlorine,<sup>1</sup> or with the smaller cylinders used mainly in laboratories.

2 The guidance is aimed primarily at managers of drum and cylinder installations, but it is also relevant for plant supervisors, design and maintenance engineers, and safety professionals. It refers to new sites, but the advice given should be implemented at existing sites where it is reasonably practicable to do so. The advice on training, maintenance, personal protective equipment and emergency response, applies at all drum and cylinder installations.

3 A wide range of industries use chlorine from drums and large cylinders. These include: chemical manufacture, water treatment, metal refining, effluent treatment, and the food industry. Installations vary in size: sites storing up to one tonne of chlorine are regarded as small sites; all other sites are regarded as large sites for the purposes of this guidance.

4 Chlorine needs careful handling because it is a highly toxic (see Appendix 1) and reactive substance (see Appendix 2). It forms flammable and explosive mixtures with some organic and inorganic substances. When released from containment, it forms a gas cloud that is heavier than air and which maintains contact with the ground as it disperses, thereby endangering people in its path. Despite the serious toxic and reactive hazards, and the potential to harm people off-site, the chlorine industry has established a very good safety record. This has been achieved through the development and practice of effective procedures for handling chlorine safely. This guidance is issued to help maintain and enhance that record.

# Management of health and safety and risk assessment

5 Employers have a legal responsibility under sections 2 and 3 of the Health and Safety at Work etc Act 1974 (HSW Act)<sup>2</sup> to ensure, so far as is reasonably practicable, the health and safety of their employees and others who may be affected by their activities. Other persons, such as designers, installers and suppliers, also have similar duties under the HSW Act with respect to products. Since 1974, various regulations have been made requiring specific controls for particular hazards (eg pressure systems etc), or activities (eg manual handling etc). A list of these and other current health and safety legislation, codes of practice and guidance is published annually.<sup>3</sup> This list also covers amendments to the regulations. References in this document are to the base regulations. Appendix 3 gives an overview of the main legislation and regulations relating to the safe handling of chlorine.

6 You must obtain planning permission for new installations in the usual way from the local planning authority, who will, when appropriate, refer to HSE for advice. If you store, or plan to store more than ten tonnes of chlorine, your site will be subject to a number of specific regulations.

7 The Notification of Installations Handling Hazardous Substances Regulations 1982<sup>4</sup> require you to notify your activity to HSE if more than ten tonnes of chlorine is liable to be kept. Subsequent changes to your activity must also be notified. New installations over ten tonnes chlorine capacity, or proposals to increase the notified capacity to more than three times the original capacity, must be notified three months in advance. The form of the notification is in the Regulations.

8 The Control of Industrial Major Accident Hazards Regulations 1984<sup>5</sup> also apply to sites storing or processing chlorine. These Regulations apply at two levels, but drum and cylinder installations will not usually be sufficiently large to be subject to the more stringent upper level requirements. The lower level requirements apply to sites which store ten or more tonnes. They also apply at sites where chlorine is involved in a process in any quantity, unless the process operation is incapable of producing a major accident hazard. You need to comply with two general requirements:

- to demonstrate to HSE, at any time, that major accident hazards have been identified and adequately controlled; and
- to report any major accidents to HSE.

These Regulations will be replaced in February 1999 by the Control of Major Accident Hazard (COMAH) Regulations which implement the requirements of the Seveso II Directive<sup>6</sup> on the control of major accident hazards; the threshold for the lower tier requirements is ten tonnes, and 25 tonnes for the top tier (see Appendix 3).

9 The Planning (Hazardous Substances) Regulations 1992<sup>7</sup> apply to sites with ten or more tonnes of chlorine. Under these Regulations, the 'consent' of the local Hazardous Substances Authority (HSA) is needed for the presence of chlorine in such quantities. The HSA must consult HSE on the associated risk levels. To quantify the off-site risks, HSE may request technical information about the installation.<sup>8</sup> 10 In addition, any process which involves the manufacture or use of chlorine or any process which is likely to result in the release of chlorine into the air or water, is a prescribed process under the Environmental Protection (Prescribed Processes and Substances) Regulations 1991.<sup>9</sup> Other processes are also prescribed in the Regulations. Under the Environmental Protection Act 1990<sup>10</sup> no person shall carry on a prescribed process except under an authorisation granted by the enforcing authority and in accordance with the conditions in the authorisation. Applications for the authorisation of a prescribed process in England and Wales must be made to the Environment Agency (EA) and in Scotland to the Scottish Environmental Protection Agency (SEPA). In addition, in Scotland where the Alkali and Works Regulation Act 1906,<sup>11</sup> as amended by the Health and Safety (Emissions into Atmosphere) Regulations 1983,<sup>12</sup> is still in force, such processes are listed as scheduled works and must be registered annually with SEPA.

11 If you transport containers off-site, you will need to comply with the Carriage of Dangerous Goods (Classification, Packaging and Labelling) and Use of Transportable Pressure Receptacles Regulations 1996,<sup>13</sup> and the Carriage of Dangerous Goods By Road Regulations 1996<sup>14</sup> (in the case of transportation by road). The relevant legislation is outlined in an HSE booklet.<sup>15</sup> (*Note: the 'legal term' for gas cylinders is now 'transportable pressure receptacles'.*)

12 Although you must comply with health and safety legislation, regulatory control cannot compensate for deficiencies in the way that safety is managed. Effective health and safety management is mainly about management (at all levels) taking a proactive approach to minimise the chance of incidents occurring, rather than putting things right after they have gone wrong. Guidance on effective health and safety management is given elsewhere<sup>16,17</sup> which advocates and elaborates on the following general principles of good management practice:

- set your policy and demonstrate commitment to it;
- organise and train your staff to ensure effective communications, cooperation, and their competence to control risks;
- plan what you need to do, set performance standards, and establish systems and procedures for controlling risks;
- measure your performance to assess whether the risks are being adequately controlled; and
- conduct safety audits to ensure that your systems are working as intended; review your findings and take any corrective action.

A risk assessment is essential to this proactive approach to safety management and is a statutory requirement of the Management of Health and Safety at Work (MHSW) Regulations 1992.<sup>18</sup> Guidance on these Regulations and risk assessment is contained in an Approved Code of Practice (ACOP).<sup>19</sup>

#### **Risk assessment**

13 The MHSW Regulations require you to conduct a full risk assessment to identify all the hazards and assess the associated risks. The risk assessment needs to include all sources of hazards, including those associated with transport around the site, access to plant and security. The need for risk assessment is also a requirement of other regulations (eg The Control of Substances Hazardous to Health Regulations (COSHH) 1994<sup>20</sup> and the Fire Precautions (Workplace) Regulations 1997).<sup>21</sup>

14 In outline, a risk assessment for your chlorine operations requires you to:

Iook for the hazards, ie potential sources of chlorine releases;

- decide how serious each of these loss-of-containment events could be, ie who could be harmed and how seriously;
- decide the likely frequency of each of these hazardous events;
- evaluate the associated risks and consider whether the precautions to prevent releases of chlorine and to mitigate their effects are adequate, or if more should be done (this guidance and the sources of advice listed in Appendix 4 are relevant here, particularly the publications of Euro Chlor);<sup>22</sup>
- record your significant findings (this is a statutory requirement if you have five or more employees); and
- update your risk assessment at least every three years, and before making significant modifications. Check that your operational experience accords with any significant assumptions you made in order to carry out your risk assessment. Safety audits, as well as day-to-day management arrangements, should address this need to check assumptions.

15 Each site will have its own special features and these need to be taken into account when conducting your risk assessment. A proper risk assessment will help you to:

- decide whether the risks are being controlled so far as is reasonably practicable; and, if not, to
- establish adequate controls and safe working procedures based on the advice in this note.

16 Your risk assessment will need to consider the main potential causes of releases of chlorine. For drum and cylinder installations these are:

- mishandling; including dropping of containers, and damage to pipework and valves during connection and disconnection of containers;
- incorrect operation; including failure to tighten joints, over-tightening of joints, failure to close valves when removing containers, incorrectly fitted joint rings, and the use of hydrocarbon lubricants which may burn when attacked by chlorine (see Appendix 2);
- failure through deterioration of plant due to inadequate maintenance, for example by corrosion or use beyond the recommended life (eg inadequate replacement of flexible connectors);
- damage by external sources (vehicles, hoists, flying debris from nearby accidents, fires etc).

17 The people conducting your risk assessment must have relevant experience and knowledge. If necessary, you must<sup>18</sup> seek assistance from experienced and knowledgeable persons. Your chlorine supplier will be able to identify competent persons able to conduct the risk assessment on your behalf, and supply information to help you carry out your risk assessment and to manage safety. The remaining sections of this publication provide guidance on the arrangements for prevention and mitigation of chlorine leaks and spillages through good design, operation (including emergency procedures) and maintenance. Sources of advice and information are listed in Appendix 4.

# Design and location of installations

#### **Types of installation**

18 Your chlorine supplier must ensure that the design, filling, maintenance, testing and examination of drums and cylinders meet the requirements of the Carriage of Dangerous Goods (Classification Packing and Labelling) and Use of Transportable Pressure Receptacles Regulations 1996,<sup>13</sup> and relevant standards, eg BS5045<sup>23</sup> and BS5355.<sup>24</sup> From 1 July 2001, the in-service examination and filling operations carried out by suppliers will need to satisfy the requirements of an approved document, known as the Approved Requirements for Transportable Pressure Receptacles.

19 Drums and cylinders meeting these requirements may be used in various types of application:

Single cylinder or drum arranged to deliver gas

This type of installation is physically capable of only a low steady rate of supply (about 1 kg/h for a 33 kg cylinder to around 5 kg/h for a drum at 15°C) or an occasional short period at a higher supply rate. If the supply rate of chlorine from a container is excessive, condensation or frosting may appear on the outside of the container, indicating that one of the methods below is more appropriate.

Multiple cylinders or drums arranged to deliver gas

If a higher demand (ie more than 5 kg/h) is expected, several containers can be connected to a common manifold. It is recommended that no more than six cylinders or drums are connected in this way. It is important to establish operating procedures to safeguard against passage of chlorine in significant quantities between containers. This may occur when one vessel is at a significantly different temperature from the others, for example, when exposed to a cold wind (in-flow from warmer containers or direct sunlight (outflow to cooler containers). If you suspect that containers are almost full, they should not be isolated (except in an emergency). If a container which is full of liquid chlorine is isolated and then becomes significantly warmer, it could rupture or distort due to hydraulic pressure (see Appendix 2). You should seek advice on the most suitable arrangement from the proposed supplier at the planning stage.

#### Drums arranged to deliver liquid

This arrangement usually serves a vaporiser in order to supply chlorine gas at a higher rate than is possible from either (a) or (b). It is also more complex and requires greater safeguarding (eg chlorine detectors linked to automatic isolation valves on the drum - see paragraph 59) because the mass release rates from pipework carrying liquid are significantly greater than those for the same hole in pipework carrying gas. This system should never be arranged to draw liquid chlorine from more than one drum at a time, unless measures are taken to keep the container at the same temperature and to prevent their isolation (except in an emergency). These measures are needed to prevent the risk of accidental transfer of liquid chlorine between vessels, leading potentially to overfilling and vessel rupture (see (b) above). To ensure continuity of supply in (b) or (c) above, a changeover panel (see Figures 1 and 2 respectively) can be provided to switch over automatically to fresh vessel(s) when the pressure in the supply vessel falls to a pre-set pressure. This pressure has to be sufficiently high to prevent suck-back; a set pressure of 1 bar gauge or more is usual.

To prevent re-liquefaction of chlorine in the pipework, it is good practice to install a pressure reducer immediately after the gas take-off point from a drum or cylinder and always after a vaporiser. Localised re-liquefaction occurs when the ambient temperature is less than the saturation temperature corresponding to the pressure of the chlorine gas. For example, if the gas is at 6 bar absolute pressure, the corresponding saturation temperature is about 20°C (see Appendix 2, Figure A2.1). If the pipework temperature is somewhat lower (eg 15°C) re-liquefaction may occur. Any liquid chlorine will increase the risk of internal corrosion. It will also tend to re-vaporise and the latent heat of vaporisation will be taken from the pipework, which then cools. Moisture will condense on the cold pipework, and present a risk of localised external corrosion. Therefore, if a pressure reducer is not fitted, it is strongly recommended that the temperature of chlorine process rooms is at least 5°C higher than that of the storeroom to prevent re-liquefaction.

21 Installations of type (a), (b) and (c) in which chlorine exists at a pressure greater than 0.5 bar gauge will form a 'pressure system' as defined in the Pressure Systems and Transportable Gas Container (PSTGC) Regulations 1989.<sup>25</sup> Pressure systems include the pipework, equipment and protective devices attached to a transportable pressure receptacle. Consequently, the design, installation and operation (including periodic examination and maintenance) of the pressure system will need to meet the requirements of the PSTGC Regulations. Guidance on the PSTGC Regulations is contained in an ACOP<sup>26</sup> and in HSR30<sup>27</sup>; see Appendix 3 for brief details. The Regulations do not apply to systems operating at or below pressures of 0.5 bar gauge.

22 Some installations are designed to operate at below atmospheric pressure. The demand valve is mounted directly on the container and arranged so that it opens only under vacuum, so the PSTGC Regulations do not apply. Such installations are inherently safer, as any leaks will in principle be inwards, and the chlorine supply may automatically (see paragraph 59) be isolated if suction is lost. This is an important consideration, as such systems usually require fewer safety features downstream of the container room. When designing and operating this type of system you need to consider:

- pressure equalisation times on start-up and shutdown. Long vacuum lines will increase this time and should be avoided (see also paragraph 28);
- a secondary containment system for long runs of pipework through enclosed process areas;
- on shutdown, isolating the chlorine supply before the vacuum ejector is turned off;
- arrangements for rapid detection and isolation of leaks, as the ingress of moisture can lead to rapid corrosion (see Appendix 2).







Figure 2 Drums arranged to deliver liquid to a vaporiser

#### **Design and location of the installation**

23 In designing your installation and operational procedures you should give special consideration to the following key features of drum and cylinder installations:

- joints to flexible or adjustable connections which are made and unmade regularly are potential sources of releases. Safe systems of work are needed to ensure that the joints are made correctly and unmade safely;
- the absence of instrumentation on the containers, so that special care is required to avoid accidental transfer of contents, resulting in overfilled receptacles and possible distortion or vessel rupture due to temperature changes should the vessel be isolated (see also paragraphs 19(b) and (c));
- the absence of a relief valve or an expansion relief vessel; it is therefore essential to avoid direct heating of the container or pipework which could cause overpressure. If 'padding' is used, a system of working is needed to avoid subjecting the containers to overpressure. ('Padding' is the use of dry air or other gas to drive liquid chlorine out of containers fitted with dip-pipes, ie drums.)

24 Small spillages of liquid chlorine are likely to evaporate rapidly. Chlorine vapour, being denser than air, tends to settle, flow along the ground and collect in low-lying areas. When the vapour is sufficiently diluted with air, the chlorine and air mixture travels with the airflow, diluting further as it does so. You need to take these characteristics into account when deciding the location of the chlorine storage area and processing equipment, and establishing procedures. For example, rooms which are below ground level and near a chlorine area should not be used as workplaces, because dispersing chlorine vapour could accumulate in such locations and present a hazard to personnel.

#### Container storage areas and chlorine rooms

25 Chlorine containers should be stored and used away from work areas. Containers may be stored:

- outside in a designated area;
- in a separate building; or
- in a storeroom which is part of another building.

In particular, containers must not be allowed to stand in water because wet chlorine is extremely corrosive (see Appendix 2) to most metals and a slight leak may rapidly escalate into a significant one. Containers should therefore not be stored or used where water might collect, eg below ground level (see also paragraph 24), in basements or near drains.

26 Outdoor storage of drums and cylinders not in use should be secure and under cover to keep off rain and radiation from the sun. The boundary of an outdoor storage area should be at least 5 m away from flammable materials. The need to provide fire protection and precautions should be considered in your risk assessment.<sup>18,21</sup>

27 The vast majority of storage areas are indoors, so that containers can be kept dry, secure, and at steady temperatures. Indoor installations also mitigate accidents by reducing the rate at which chlorine is released to the environment. They are strongly recommended in areas with relatively high densities of people off-site, or where installations are near to hospitals, schools or other sensitive populations. (The advantages and disadvantages of indoor and outdoor installations are discussed in Appendix 5.) Wherever possible, you should locate rooms for storage or use of chlorine at ground level (see paragraph 25). Indoor storage areas and rooms in which chlorine containers are used, should be constructed of substantially non-flammable materials and provide shielding against radiant heat in case of fire nearby.

28 To avoid the need for long runs of pipework, the equipment using chlorine should be located close to the storage area, preferably in a building which could also house the storeroom. It is strongly recommended that a connected-up container is not in the same room as the equipment being fed by chlorine, or equipment being used in other processes.

29 The storage area needs to be clearly identified and marked<sup>28-32</sup> (see also Appendix 3, Dangerous Substances Regulations, 1990). It should be used solely for the storage of chlorine, associated essential equipment, and compatible materials such as sulphur dioxide. The chlorine area should be secured against unauthorised entry. Access to the store should be limited to authorised personnel.

30 Access doors should fit closely to help contain any leak (see also paragraph 114), have a crash-bar escape facility and an observation window. At unstaffed remote sites, an observation window need not be fitted for security reasons. Internal doors leading from the storeroom to other workrooms are not recommended; when fitted they need to have air-tight seals so that minor leaks can be confined. Any pipework and cable ducting between adjoining rooms should be suitably sealed for the same reason. Control switches for lighting and ventilation should be located outside the chlorine room.

31 You need to provide adequate escape routes. To allow workers a ready means of escape in an emergency, chlorine rooms need to be positioned on the 'outside' of a building so that they lead directly to open air. Escape doors and gates on these routes should open in the direction of escape and be fitted with pushbars. Escape routes and doors should be marked with luminous markings to enable identification in the case of power failure. The local fire authority should be able to advise on the choice and marking of escape routes when you consult them about emergency planning (see paragraphs 106-110).

#### Location of chlorine store and process rooms

32 The chlorine area (see also paragraphs 28 and 29) should not be closer than 5 m to a roadway used by vehicles, unless you provide adequate protection barriers (eg crash barriers or substantial walls). If the walls of the store or rooms are intended to provide impact protection, you should design them so that they will not collapse and damage the installation. Where vehicles have access into a store for loading and unloading, you should provide high kerbs or other fixed wheel stops. In addition, you should consider arranging the loading and unloading points to allow vehicles to 'drive through' without the need to reverse. Dedicated loading/ unloading areas should be clearly marked (see also paragaph 29).

33 Suitable separation of the store and process plant from the site boundary gives a good measure of protection to people off-site against significant chlorine releases such as the failure of pipework carrying liquid. It also affords worthwhile protection against the rare but larger-scale incidents involving damage to the container. The size of such separation distances will depend upon a number of factors including:

- the total inventory of chlorine stored;
- whether the storage is indoors or outside (see paragraph 27);
- the rate of consumption;
- the frequency of drum and cylinder handling/movements on-site;
- the design of the installation, eg length and diameter of liquid and vapour lines, the number of containers on a manifold; and

the size, distribution, and type (eg sensitive groups) of the surrounding population.

34 You should carefully consider these factors when designing and deciding the location of your installation and when conducting your risk assessment (see paragraphs 13-17). These factors also apply when considering relocation of an installation within a site; you should involve your chlorine supplier at an early stage. Consideration should be given to maximising the distance between the site boundary and the on-line cylinders, drums, or equipment.

35 The following are indicative of separation distances to the site boundary that have been found to be reasonably practicable for some indoor installations:

- for installations using cylinders only, 20 m;
- for drum installations with about 10 tonnes on site:
  - 60 m for the drum unloading area and the drum store;
  - 60 m for on-line drums arranged to deliver liquid; and
  - 40 m for on-line drums arranged to deliver gas.

It should be emphasised that your risk assessment and individual circumstances (site location, space available on-site, site surroundings, frequency of container changes, inventory etc) will determine the separation distances. For similar circumstances outdoor installations may require larger separation distances (see paragraph 27).

36 When choosing the location for your chlorine area, the location of other on-site buildings in relation to the prevailing wind direction needs to be considered. It is recommended that the chlorine area should be located downwind of buildings that are regularly occupied. Ventilation intakes to occupied rooms should be at least 25 m from the chlorine installation, and preferably at a high level. You also need to take account of the prevailing wind direction when deciding the locations of emergency assembly points. Two assembly points are recommended; these should be located so that at least one will be available, regardless of the wind direction when a release occurs. For extensive sites, indoor assembly points are recommended; open-air assembly points are suitable for simple sites.

#### Good practice in the handling and use of drums and cylinders

37 Your procedures and arrangements for handling and connecting containers to equipment should address the following:

- Drums and cylinders should be used in the order in which they are delivered to minimise the risk of the valves seizing.
- Containers should be visually inspected on receipt and before connection. Containers which you suspect are defective should not be used and should be labelled as defective. You should promptly notify any defect to the supplier so that their procedure for dealing with defective containers can be initiated.
- Containers should be secured in their working position before being connected to other equipment. Drums should rest directly on properly designed chocks or cradles, and should not be double stacked on drums in use. Where roller cradles are used to support drums, the drums should be secured in position with chocks or ratchet strap assemblies. Cylinders should be secured upright, preferably in purpose-designed clamps.
- The need for care in handling containers to avoid dropping them.
- The need for care in handling loads to avoid dropping them on containers.
- Cylinders should be transported in the workplace using purpose-made cylinder trolleys or stillages. Any changes in level should be via ramps rather than steps.
- Fork-lift trucks should not be used for moving containers, unless purpose-

made attachments are fitted.

- Operations requiring the raising of drums high above ground level should be minimised. Raised drum decks or lowered access platforms for lorries are recommended.
- The adequacy of the arrangements for handling containers should be assessed annually (see also paragraph 93).

Your chlorine supplier should be able to provide additional guidance on the safe handling of containers.

38 Lifting equipment needs to be properly designed for the envisaged duty and maintained and tested in accordance with the manufacturer's instructions. For new installations, you should arrange the hoist so that loads do not pass over chlorine drums, drum valves and associated pipework which are on-line, ie the drum-outlets should point towards the nearest external wall (face 'outward') in buildings which have a central lifting beam/runway. If this is not possible at existing installations, your procedures need to keep to a minimum the number of occasions where drums pass over on-line equipment.

39 Lifting beams for chlorine drums should have a minimum reach of 2 m. Hoists should be capable of slow speeds of operation to minimise swinging loads; speeds of about 1m/min for vertical movements and 4.5m/min for horizontal movements have been found to be suitable. Guide ropes may be needed to prevent the drums from swinging.

#### Ventilation

- 40 Ventilation of chlorine storage rooms serves three main purposes:
- to maintain 'fresh air' and a suitable working environment;
- to disperse minor leakages after they have occurred in an enclosed room;
- to provide controlled containment and dispersion in cases of significant leakage.

You can provide fresh air to the storage room either by natural ventilation or by forced ventilation. Natural ventilation can be supplied through louvres (powered or unpowered) at high and low level. Airbricks are adequate for small storerooms and should provide at least two air changes per hour. Airbricks are not recommended at large installations as they are difficult to seal in an emergency. At larger installations forced ventilation, by means of an exhaust fan and ductwork, is preferable. At all sites where a chlorine room opens off another room or corridor and does not directly open to outdoors (see also paragraph 30), forced ventilation with automatic or semi-automatic controls is strongly recommended.

41 When designing forced ventilation systems you should ensure thorough ventilation of the room and the elimination of any pockets of still air. Typically at least six to ten air changes per hour are needed. The actual requirement will depend on the size of the room, the layout of equipment within it, and the judgement about the maximum release rate that can be mitigated by forced ventilation. You should discuss your requirement with your chlorine and equipment suppliers. Automatic control of the fans and louvres, with manual override, is recommended at larger installations. You should be located outside the chlorine room and should be clearly labelled. It is good practice to interlock the louvres to the fan motor control and arrange for them to close when the fans are not in use, or when

shut down by the gas detection system (see paragraphs 45-50).

42 At larger installations, particularly those with ten or more tonnes of chlorine, consideration should be given to the provision of gas-tight doors, powered ventilation louvres and venting to a fume scrubber (see also paragraph 81). Such protection should be provided if there is a school, hospital or an appreciable number of houses in the vicinity.

43 The ventilation arrangements should be subject to a routine maintenance regime. This could include a simple weekly check on the ventilation efficiency with more formal maintenance checks with logging of results performed monthly. Where ventilation systems have been installed as part of a control measure to prevent the exposure of operatives to chlorine under the Control of Substances Hazardous to Health Regulations (COSHH) 1994,<sup>20</sup> a thorough examination and test of the ventilation system, and full operating efficiency tests must be performed at least once every 14 months. You must record the results of such examinations and keep them for at least five years.

44 If there is a build-up of chlorine in a workroom (as opposed to its transient presence during drum/cylinder changeover) to the level (about 0.5 ppm) that can be detected by smell then it should be assumed that there is a plant fault. You should not rely on good ventilation to create a safe working atmosphere. An increase in leakage rate could quickly render the space unsafe even for brief exposures. To deal with leaks, breathing apparatus must be worn (see paragraphs 111-118).

#### **Chlorine detectors and alarms**

45 An early warning of chlorine leaks, particularly in buildings which are not continuously staffed, has the advantage of allowing prompt remedial action. Installation of chlorine detectors and alarms in buildings housing chlorine drums, cylinders, vaporisers or process plant is therefore strongly recommended. For outdoor installations, you should assess their value by considering factors such as the size of the installation, the staffing levels and the response times achievable. On detecting a leak the detector should:

- raise an audible alarm in a continuously staffed area or control centre;
- activate audible and visual alarms in the affected area;
- control the mechanical ventilation, if fitted; and
- operate the automatic isolation valves, where fitted.

46 Audible alarms need to have a distinct tone; in addition, warning lights of the amber flashing or traffic light type may be fitted outside each chlorine building. Where appropriate, for example at large, remote or sensitive sites, alarms should be connected to a telemetry system to provide warning at a staffed control point. The control point should be able to isolate the chlorine supply, preferably via a remotely operable valve fitted to the cylinder or drum. For sites staffed by lone workers, you should consider providing portable alarms and communication systems in addition to any fixed alarms.

47 Typically, chlorine sensors need to be located in or near the entrance to ducts carrying chlorine pipework, the air intakes to extractor fans and at the outlets from fume scrubbers (see also paragraph 55). Where forced ventilation systems have been installed, the detector should be located at the outlet of the system; where this is not reasonably practicable, the detector should be placed near the storage and use areas. In a store where 'still air' pockets could exist, a fan should be used to improve the general air circulation, and the effectiveness of any detection system. The manufacturer or supplier of your system should advise on

the best location for the sensors; typically sensors in the storage area are mounted between 0.3 m and 0.5 m above ground level. You should arrange for chlorine gas sensors to be tested regularly in accordance with the manufacturer's instructions and to demonstrate that the detector and its associated circuits are functioning correctly. You should keep records of the results of the tests.

- 48 Detection systems need to:
- provide a continuous monitoring function when chlorine is in storage or in use;
- operate the alarms in the event of power loss, sensor failure, or low condition of the stand-by batteries; and
- have battery back-up protection for all alarm relay operations.

49 The detector system should activate the low level alarm at a chlorine concentration of 1-5 ppm. Lower settings are liable to activate the system at every drum/cylinder change, unless a duration requirement is also imposed. For example, some companies set the low-level alarm at 0.5 ppm, but require the sensor to register this concentration for at least 30 seconds, to avoid spurious trips of the alarm system during the changing of containers. The low alarm level should activate the ventilation fan, open the intake louvres, and activate the local audio and visual alarms and any remote telemetry alarm.

50 Multi-stage detector systems are sometimes used to give an indication of the severity of the malfunction to personnel outside the chlorine room. These systems are recommended at larger installations. It is suggested that the highlevel alarm operates at about three times the level of the first-stage alarm, ie 3-15 ppm, depending on the duration that the sensor needs to register this level. Some companies set the high-level alarm at 2 ppm with a 30 second duration requirement. On activation of a high-level alarm the detector system should also shut off the ventilation system and operate the auto-shutdown system (where fitted, see paragraph 59). The tone of the alarm at low and high levels should be different and operators should be trained to recognise the difference and how to respond in each case. Local alarms may be supplemented by telemetry links to control rooms, where appropriate. The response to alarms is covered in paragraphs 106-118.

51 Some sensors can be damaged by high chlorine concentrations; detector systems should therefore be checked following any high level alarms (see also paragraph 115).



Ventilation/extractor fan



Chlorine detector located close to the fan inlet. The fan is activated by the low level alarm and deactivated by the high level alarm



The fan control unit is located in a separate room

#### **Pipework**

52 Any pipework conveying chlorine from a cylinder or drum at a pressure greater than 0.5 bar gauge will form part of a 'pressure system'. Its design and installation must therefore satisfy the requirements of the Pressure Systems and Transportable Gas Containers (PSTGC) Regulations 1989.<sup>25</sup> The pipework between the supply container and the point of use needs to be robust and as short as is practicable. It should be sited so as to avoid impact or be suitably protected against mechanical damage. Routing of pipework for liquid chlorine should normally be above ground. Where long pipework runs are unavoidable, as much of the run as possible should convey low-pressure gas rather than high-pressure gas or liquid. Long lengths of liquid-filled pipework require a suitable pressure relief system, for example in the form of an expansion chamber with rupture disc (see Figure 3). You should not use plastic pipework for liquid chlorine or chlorine gas under pressure.

53 You should ensure that all pipework and screwed fittings are designed and manufactured to recognised standards. Pipework carrying liquid chlorine or chlorine gas under pressure should be constructed in accordance with a recognised code such as ANSI/ASME B31.3.<sup>33,34</sup> Screwed fittings need to meet BS21<sup>35</sup> standards. The design pressure should be not less than 12 bar gauge (174 psig) and the recommended design temperature range should be -35°C to +45°C. The adequacy of the design should be considered as part of your risk assessment which may include a HAZOP<sup>36</sup> study.



Figure 3 Pressure relief system for chlorine pipelines

54 New steel pipework should be pressure tested to at least 12 bar gauge using dry (dew point less than -40°C) air, nitrogen or any other suitable gas. Any

leaks should be rectified as part of the commissioning procedure. Any part of the system which may operate above 45°C should be designed to withstand the corresponding vapour pressure of chlorine (see Appendix 2, Figure A2.1). As with other parts of the installation, pipework should be subject to routine inspection and maintenance. Any records of the examination report under the Pressure Systems and Transportable Gas Container Regulations 1989<sup>25</sup> must be kept for at least five years (see Appendix 3 for more details). All pipework should be kept clean and dry inside. After any exposure to moisture, or hydraulic test, the pipework must be thoroughly dried (dew point less than -40°C) and joint rings should be changed.

55 For chlorine gas at atmospheric pressure or below, suitable plastic pipework (eg UPVC of the appropriate grade) may be used. However, you should seek advice from a supplier of plastic pipework on its suitability for your application. This advice needs to include procedures for the installation (eg suitable clips to allow expansion/contraction), inspection and maintenance, replacement of the pipework, and take into consideration the possibility of impact damage and other hazards. You need to test the integrity of the installation prior to service. If your installation is equipped with a vacuum regulator, fitted with a vent to atmosphere, the discharge vent needs to be labelled and directed to a safe place (see Figures 1 and 2). You should also consider locating a chlorine detector at the exit of the vent to provide early warning of a leak.

56 The use of incorrect materials for gaskets can be dangerous; if in doubt, you should seek the advice of your chlorine supplier. Rubber gaskets should never be used for liquid chlorine service. All packings, gaskets and diaphragms should be resistant to the action of chlorine between the extremes of operating temperatures and pressures. Proven materials such as spiral wound Monel, Kel-F or Aramid fibre are suitable. Some users have found lead gaskets to be suitable, although they are sometimes difficult to remove and replace. Compressed asbestos fibre (CAF) gaskets to BS 1832,<sup>37</sup> grade A or O, preferably graphite-treated on each face to facilitate dismantling, are suitable for joints that are expected to remain in service for several years without being disturbed. Any used asbestos components should be collected and disposed of safely. Where joints are made and remade relatively frequently, CAF is not recommended for environmental reasons. Alternative jointing material such as aramid fibre should be used. Polytetrafluoroethylene (PTFE) to BS 6564<sup>38</sup> grade UA 1/1 may be suitable, provided the joint is of an encapsulated type, eg a spigotted joint to prevent the PTFE 'creeping'. Where a variety of gasket materials are used, joints should be tabbed for easy identification. Manufacturer's instructions need to be strictly adhered to. Over-tightening fittings should be avoided, as this can result in leaks due to the subsequent failure of the fixing nuts or packing.



Testing for leaks following connection of the pigtail to the drum's gas take-off valve

- 57 You should make arrangements to ensure that:
- an adequate supply of suitable jointing material is available at all times and that gaskets and other jointing material are never re-used;
- you only use lubricants recommended for use with chlorine; never use hydrocarbon-based lubricants as they react with chlorine and may ignite and cause a chlorine-iron fire with subsequent loss of containment;
- suitable tools are readily available and used when making joints; adjustable wrenches are not recommended; and
- newly-made joints are tested for leaks with an ammonia bottle. A leak is indicated by the formation of white fumes of ammonium chloride (this is a sensitive and well-established test).

58 Flexible pigtail connector pipes are often made from copper or alloys which are subject to work hardening. They need to be inspected visually at each drum or cylinder change and replaced if necessary. You should develop a planned replacement programme in conjunction with your supplier. For the programme to be effective it is recommended that flexible connectors be tagged with an installation and renewal date and a recorded inspection schedule. The renewal date needs to take account of the working life of the component. Where connections and disconnections are frequent (two or three container changes per month), copper and alloy connectors need to be replaced at least annually. Mild steel pigtails have a much longer life. Replacement and inspection intervals will depend on the duty and should be recorded in the maintenance schedule or, if necessary, in the written scheme of examination (see paragraph 84). Measures need to be taken to prevent localised liquefaction of chlorine in connectors and pipework (see paragraph 20).

#### Valves and automatic shut-off devices

59 Euro Chlor<sup>22</sup> produce a number of publications on the use of different types of valve. Ball valves are commonly used at drum and cylinder installations, though at larger installations globe valves are recommended, especially for key isolation duties. Valves used for emergency isolation need to be marked (see paragraph 60). You should address the need for remotely operable or automatic valves in your risk assessment. The need for an automatic system will depend on the likelihood, size and duration of potential leaks and the proximity of off-site populations and sensitive developments such as schools, hospitals etc (see also paragraph 33 and paragraphs 72-75). Remotely operable and automatic shut-off devices should be installed directly onto the drum or cylinder valve, so that in the event of a leak the package valve can be closed. Automatic shut-off devices should be activated by the chlorine detection system (see paragraphs 45-51) and, for multi-stage detectors, it is the operation of the high-level alarm which activates valve closures. Operating points for remotely operated valves and manual override controls for automatic valves should be located outside the control room, and possibly at other places identified in your risk assessment. Automatic and remotely operable valves need to be tested regularly, for example at weekly intervals, and the results recorded.

#### Marking

60 It is recommended that chlorine pipework should be clearly labelled and painted yellow in accordance with BS 1710<sup>39</sup> (eg to 08E51-BS 4800<sup>40</sup>). The Health and Safety (Safety Signs and Signals) Regulations 1996<sup>30</sup> require clear labelling whenever risks to employees cannot be avoided or adequately reduced by other means; advice is given in the associated guidance.<sup>31</sup> It is good practice to mark valves which are required to operate in an emergency with a clear indication of their function and the direction in which they open and close. These markings need to be consistent with the markings on any flow diagrams or operational instructions. Valve keys for operating the emergency valves should be located near to the valve.

#### **Protection against corrosion**

61 Equipment (including connections, fittings and pipework) needs to be adequately protected against corrosion by protective coatings such as paint or other means. Areas where moisture may collect (for example pipe-lagging) will need special attention. Water pipelines to and from equipment such as vacuum ejectors should not be run through storage areas because they promote condensation and subsequent external corrosion as well as being a source of leaks. Routine inspections need to take account of how well the corrosion protection is performing; any deterioration needs to be recorded and rectified.

#### Vaporisers

62 Vaporisers (also known as evaporators) are used to convert liquid chlorine into gas. A plant with a low rate of use of chlorine can draw the gas straight from containers. Flow rates from about 1 to 25 kg/h are possible depending on the container size and the number that are manifolded together (see paragraph 19b). Higher rates (more than about 25 kg/h) require a vaporiser to convert liquid chlorine from a drum into gas. Otherwise there is the risk of process liquids passing back into the drum, or irregularity of gas supply (see paragraph 19 (b) and (c)). The need for a vaporiser should be discussed with the proposed chlorine supplier at the design stage. (*Note: Cylinders are unsuitable for such high demand rates and are not supplied with dip pipes*.)

63 At drum installations, cylinder or coil-in-bath vaporisers (see Appendix 6, vaporisers types 1(c) and 2) are usually used as they are essentially self-regulating. When demand is high, the liquid chlorine level rises in the vaporiser, and a greater heat exchange surface area is presented to the liquid, thereby increasing the vapour generation rate. When demand is low, the greater vapour pressure at the temperature of the heating medium drives the liquid chlorine out of the vaporiser back into the storage vessel and the evaporation rate falls.

64 The bath temperature is thermostatically controlled, usually in the range 60-70°C which is well below that at which any significant reaction between carbon steel and dry chlorine occurs. Direct electrical heating of the cylinder or coils should not be used because of the risk of local overheating. A wet steam bath is sometimes used with coil type evaporators. The steam should be at a pressure less than 2 bar gauge and not be superheated. Appendix 6 describes the advantages and disadvantages of a number of types of vaporiser.

#### **General installation**

65 The vaporiser should be installed as close as possible to the chlorine supply drum in order to keep pipelines carrying liquid chlorine short; long pipe runs will require pressure relief (see paragraphs 52-70). Changeover of the liquid chlorine supply is discussed in paragraph 19. The design should aim to:

- minimise the risk of any accidental chlorine release; and
- provide adequate access and isolation facilities for maintenance and emergency action in the event of an incident.

#### **Hazards**

66 Potential hazards associated with chlorine vaporisers include:

- pinhole leaks, leading to rapid corrosion and increased loss of chlorine;
- rapid corrosion, if any moisture is allowed into the chlorine system;
- reverse flow of reaction fluids, caused by a fall in pressure in the vaporiser, or by excess pressure in the process, or by solution of chlorine gas in the fluid.

The presence of the fluid (water, solvent or reagent) in the vaporiser can cause corrosion or local violent reaction leading to rapid overpressure and possible vessel rupture;

- carry-over of liquid chlorine as bulk fluid or droplets into the gas line or into the process itself. This can, depending on the materials of construction and on the process, cause damage or hazard;
- excessive gas pressure to the system due to overheating a vaporiser, since the vapour pressure of chlorine rises very steeply with temperature (see Appendix 2, Figure A2.1); and
- excessive hydraulic forces if the system is closed up and full of liquid due to the expansion of liquid chlorine when heated.

These basic hazards are considered in more detail below, but grouped according to the type of hazard.

#### Flooding and liquid carry-over

67 Flooding (filling) of the chlorine vaporiser with liquid chlorine may result from operation of the equipment above its capacity, inadequate heating, or fouling of the heat transfer surfaces. You should consider installing a gas flow rate indicator. This may be of value to the operator for routine purposes, and will also indicate excessive withdrawal rates. The temperature of the heating medium is usually controlled thermostatically. If the temperature of the heating medium falls too low in a self-regulating evaporator, it is possible for the outgoing gas to be inadequately superheated, or for flooding to occur. Flooding results in carryover of liquid chlorine into the vapour lines, and a potential hazard (depending on the process and plant materials). The same may happen if the level of water in a water bath falls. In the extreme, if chlorine is drawn off but no heat is supplied to the vaporiser, it is possible for ice to form on the heat exchanger surfaces and damage them severely.

68 You should consider fitting a knockout pot (or spray catcher) to prevent chlorine droplets and spray from passing into gas pipework when liquid chlorine might damage the material of the pipes, or cause the process to become unstable. In all cases where the possibility of liquid passing to process is unacceptable, it is strongly recommended that a low temperature alarm be fitted near the knockout pot and arranged to cut off the liquid chlorine supply to the vaporiser or (in selfregulating types only) the gaseous chlorine outlet may be closed, driving the liquid chlorine back into the drum(s). Adequate instrumentation and alarms should always be provided to give immediate warning of this condition. High and low bath temperature and level alarms with shutdown facilities are recommended.

#### Accelerated corrosion and reaction (high temperature)

69 To avoid rapid corrosion of the water side of heat exchange surfaces made from galvanised steel, operating temperatures should not exceed 70°C. If operation at higher temperatures is required, vaporisers made of nickel or nickel alloys (such as Monel 400 or Inconel) should be used. In such cases, the downstream chlorine gas pipework may also need upgrading to ensure adequate resistance to corrosion at elevated temperatures.

#### High pressure

70 Precautions must be in place to protect the system against overpressurisation, for example, a pressure relief device. Pressure relief devices and high pressure alarms, where fitted, need to be properly designed, installed and maintained. Devices designed to protect the system against overpressurisation must be periodically examined by a competent person.<sup>25</sup> The vapour pressure of chlorine at a typical working temperature of 70°C exceeds 21 bar (see Figure A2.1, Appendix 2). It follows that you need to take steps to:

ensure that the vaporiser is not isolated when full of liquid chlorine.

Strict observance of written procedures for shutdown is vital;

- avoid accidentally isolating the vaporiser on both sides. Care needs to be taken to ensure that the closing arrangements for the emergency valves take this into account (see paragraphs 72-75);
- design the vaporiser shell and pipes to withstand the working pressure and duty; and
- implement operational controls which minimise the risk of the working pressure being exceeded.

If your chlorine vaporiser is not supplied with a pressure relief device you will need to adopt suitable procedures, or fit suitable pressure relief, to ensure that the conditions in (a) to (d) are met. Arrangements for pressure relief need to ensure that the chlorine is contained or that discharges to vent lines are suitably processed (eg see paragraph 81).

#### Reverse flow

71 You should eliminate the possibility of suck-back into the vaporisers by suitable design. For example, water-chlorinating package systems usually incorporate a set of valves in the control system to prevent suck-back or push-back. The arrangements vary, and care needs to be taken to ensure that the system provided does give protection in the event of, for example, a leak at the ejector non-return valve. You should also consider fitting a low-pressure gas alarm to the outlet gas line. This gives warning of loss of supply to the process, and may indicate a need to initiate purging of the system, using dry air or other suitable dry gas (dew point less than -40°C) to prevent suck-back. Whatever method is used, the system needs to be regularly inspected and maintained, and adequate records kept.

#### Routine and emergency isolation

72 The vaporiser has to be capable of being isolated for maintenance, or in an emergency such as a failure of the vaporiser itself through leakage or a failure of the gas line downstream. In addition to a manual valve on the liquid inlet and on the gas outlet, remotely or automatically operable valves are strongly recommended on both inlet and outlet. A pressure-reducing or flow-control valve will almost always be fitted on the outlet and it is sometimes possible for this valve to be the remotely-operable shut-off valve.

73 Your risk assessment should consider the need for additional protection in the event that automatic valves fail to operate (or remotely operable valves are not activated) in an emergency. For example, a flow restriction in the liquid inlet (typically on the exit from the drum), will limit the release which could occur in the event of a major plant failure.

74 The hazards of total isolation of the vaporiser are considerable and will be most severe when the evaporator is full (eg if the valves close together in a condition of major gas line failure). If there is a gas space above the liquid chlorine when the vaporiser is isolated and heated, the internal pressure will reach that of chlorine at the heating medium temperature. The vaporiser, lines and valves need to be designed to withstand such pressure or relieve it to a safe place. The control of automatic valves needs to be arranged so that the valves do not close together when an alarm is raised (see also paragraph 70). One approach is to arrange for the gas control valve to close on alarms related to improper working of the system (eg low gas pressure, downstream process alarms, low temperature) and the liquid control valve at the drum to close on chlorine release (eg detectors local to the vaporiser and storage, or manual alarms). If the plant is continually staffed, manual intervention may be a suitable alternative to providing wholly automatic operation of shut-down. However, procedures need to be established to ensure that this does not introduce significant delays into the response to an alarm.

75 Isolation of the vaporiser is still possible, but interlocks between the inlet and outlet valves to prevent total isolation are rarely fitted because it is occasionally necessary to close both valves during cleaning and overhaul. A safe system of work for maintenance and operation is thus a vital part of the safety arrangements, and is a requirement under the PSTGC Regulations.<sup>25</sup>

#### **Pressure control valves**

All vaporiser designs incorporate an element of superheating of the vapour, either in the vaporiser itself or as a separate unit. This is necessary to prevent chlorine re-liquefying in the control valves, where it could cause problems of irregular pressure in operation and local external corrosion (see paragraph 20). These problems are avoided by reducing the gas pressure on exit from the vaporiser. In addition, it is recommended that a suitable pressure-reducing control system is provided.

#### Corrosion

77 Corrosion of the vaporiser tubes or coils could lead to a loss-of-containment accident. The consequence of a minor chlorine leak from the chlorine side of a vaporiser heating bath could be very serious, since the mixture of chlorine and moisture will lead to rapid corrosion of the evaporator surfaces and a substantial release of chlorine.

78 You must arrange for a competent person to periodically examine your vaporiser and other pressure systems in accordance with your written scheme of examination.<sup>41</sup> A competent person must certify that the written scheme of examination is suitable for the purpose of preventing reasonably foreseeable danger to persons from the unintentional release of stored energy from the system. The written scheme of examination should describe the nature and frequency of the examination which will depend on the duty and the condition of the vaporiser when last inspected. The competent person will advise on suitable examination and test regimes and when the vaporiser should be replaced. Examination intervals between one and five years are typical. Coil-in-bath evaporators are commonly given a rigorous inspection every two years, and the coils are discarded if seriously pitted. Chlorine evaporator cylinders should be renewed after five years. The old one may be submitted to a competent inspection body for certification for further use if required. Following examination, the equipment should be thoroughly dried to a dew point less than -40°C before recommissioning. Moisture left in the system can lead to very rapid corrosion. The procedure should be covered by a written operating procedure.

79 Corrosion of the heat exchanger surfaces is not directly monitored. Instead the evaporator vessel or tubes are frequently protected against water corrosion by cathodic protection. Typically, the anodes should be checked visually every three to six months. The frequency should be established by experience of the rate at which the anodes are consumed and replaced. If the anodes are found wholly consumed at inspection, a thorough examination of the vaporiser should be undertaken. The water bath or condensate outlet should be monitored for chlorine leaks by redox or conductivity measurements. This early warning of minor leaks is helpful in all cases, and is very strongly recommended if cathodic protection is not provided or not maintained.

80 Accumulation of solid deposits reduces the effectiveness of a vaporiser and can also enhance corrosion. The vaporiser needs to be cleaned and dried regularly; the purge gas should be oil-free and have a dew point less than -40°C. Close attention to the cleaning procedure will minimise corrosion.

#### Chlorine absorption system (fume scrubber)

- 81 The strategy for risk control places emphasis on:
- preventing loss-of-containment accidents through good design, maintenance and operation of plant; and
- limiting the duration of any release by early detection and shutdown via remotely or automatically operated package shut-off valves.

For the vast majority of cylinder and drum installations, therefore, the scale and nature of the consuming process does not warrant the additional protection of a special absorption unit. However, at larger sites, particularly those with inventories of ten or more tonnes, the need for an absorption unit should be addressed by the risk assessment. Important factors include those listed in paragraph 33. For new sites, the need should be considered at the design stage. If you conclude you need an absorption unit you should discuss your requirements with your chlorine supplier who will be able to advise on the need to involve other experts. If you decide to use an absorption system, it is essential to maintain it in good working order so that it will operate on demand. You may also need to involve the Environment Agency in England and Wales, and SEPA in Scotland, because any planned controlled emissions of chlorine to the environment from prescribed processes (see paragraph 10) must be discussed with them.

## **Procedures and training**

#### **Operating instructions**

82 One of the main risks of chlorine escape to the environment arises from incorrect operation of the plant. Operating procedures and the selection and training of process operators are therefore extremely important considerations for the efficient and safe operation of chlorine installations. Your operating procedures need to cover each process operation and meet legal requirements such as those in <sup>18, 25, 42-44</sup> and the standards recommended in industry guides (see Appendix 4 and reference 22). Written instructions are required for all routine and emergency operations. These may take different forms depending upon the complexity of the installation, for example from simple guide cards for straightforward operations to complete manuals for complex operations and installations. You should make the site manager or other designated person responsible for authorising any amendments to the procedures or schedules. You need to ensure that copies of the instructions include a flowsheet and indicate the valves to be closed in an emergency. Instructions need to be available in the working area for operators, and in the control room or control centre for operators and supervisors. Supervisors should check regularly that operations are carried out precisely according to the written instructions.

#### **Maintenance and inspection**

83 Satisfactory maintenance of plant, equipment and instrumentation is essential to minimise risks. The main Regulations that you need to comply with are: COSHH Regulations,<sup>20</sup> MHSW Regulations,<sup>18</sup> and PSTGC Regulations (regulation 12).<sup>25</sup> The CIMAH Regulations<sup>5</sup> (to be replaced in February 1999 by the COMAH Regulations - see Appendix 3) may also apply, depending on the size of the installation and the operating conditions.

84 You will need to prepare maintenance schedules defining the required frequency for servicing, testing and inspection. These schedules should be strictly adhered to. Appropriate records of the results must be kept as required by the PSTGC Regulations 1989 and COSHH Regulations. The need for a written scheme of examination (WSE)<sup>41</sup> is a separate requirement (ie regulations 8 and 9) of the PSTGC Regulations. Other aspects of maintenance are referred in paragraphs 16(c), 25, 38, 43, 54, 55, 65, 70-72, 75, 79, 81, 96 and 113).

85 You need to ensure that detailed written instructions covering all routine maintenance operations are available. These should be formally approved and issued by the responsible maintenance engineer. Supervisors should check regularly that work is carried out according to these procedures. Particular attention needs to be paid to corrosion (see also paragraphs 61 and 77-80), especially where lagging is used; and to chlorine detector systems to keep such monitoring equipment in effective operation especially in installations such as certain water treatment plants which are routinely unattended but monitored by telemetry.

86 Close liaison is necessary between the maintenance engineer and the process manager, to ensure that maintenance work is started only after the equipment concerned has been adequately prepared by process personnel and is free from chlorine.

87 Adequate training is required for all maintenance personnel. This should include basic information on the properties of chlorine, safety precautions and emergency procedures (see also paragraphs 91-93).

#### Modification of the chlorine system and clearance procedures

88 You should only modify the chlorine system after conducting a risk assessment (and possibly HAZOP).<sup>36</sup> This ensures that approval is given by responsible staff covering the operating and engineering sections involved, and that appropriate procedures are put in place to deal with any alterations required. Proposed major modifications should preferably be discussed with your chlorine supplier.

89 The Pressure Systems and Transportable Gas Containers Regulations 198925 require (regulation 4) you to make arrangements for proper control of repairs and modifications to pressure systems. Any modifications or repairs which could affect the integrity of the system have to be defined and overseen by a competent person.

90~ Formal clearance procedures need to be established as part of a permit-towork system  $^{46}$  for:

- ensuring that the plant is in a satisfactory condition for maintenance and internal examination, appropriately isolated and free from chlorine;
- covering all work in the chlorine area which requires the use of cranes, mobile equipment, welding sets or other plant which could lead to accidental damage to the chlorine system. This safeguard is necessary even if the work does not directly involve the chlorine-containing lines or equipment;
- formally accepting that the plant is safe for operation after the work has been completed.

#### Training

91 You need to ensure that site personnel are properly trained and practised in each procedure. You should develop and implement a training programme which includes both 'off-the-job' and 'on-the-job' aspects. You should regularly assess the programme for its effectiveness. *Off-the-job* training needs to include basic information on the following:

- statutory requirements, ACOPs and Guidance;
- physical, chemical, and toxic properties of chlorine;
- safety precautions;
- personal protective equipment;
- process operations and system configurations;
- safe systems of work including 'permit-to-work';
- container types, methods of handling and security;
- operational procedures;
- maintenance procedures;
- defect rectification;
- automatic control systems;
- leakage detection systems;
- emergency procedures including leakage containment; and
- chlorine suppliers' support facilities.

Maintenance engineers need to be provided with more detailed training on the above topics, together with training on system integrity testing, pressure reduction, and safety devices.

#### **General guidelines for training**

Individuals have legal duties to comply with the safety procedures associated with their work. However, it is never sufficient simply to presume that staff will know and understand what to do. Positive instruction and training is needed. Health and safety training should take place during working hours and should be part of the job.

Training is vital in helping to prevent incidents and to minimise the consequences if they do happen. Think about who should be trained, in what, and to what level of competence.

Training will help employees understand the health and safety aspects of their work. Initial training for new staff should be followed up as necessary with new or refresher training as required.

Those to be trained must include anyone who works on the site. Operators, managers, staff and occasional visitors such as maintenance contractors etc may all need some training.

Training can take many forms ranging from on-the-job training linked to information notices, written instructions etc to formal training courses. The type of training needed should be appropriate to the activities/duties of those to be trained and the hazards at the site.

Involve and consult staff. Where there is a recognised trade union safety representative they will need to be consulted. They will know many of the hazards occurring in everyday situations and should be consulted. Cater for unusual occurrences.

Information, instruction and training must be understood by those to whom they are given. If poor performance shows that training is not working, the training will need to be reviewed and improved. Do not assume that previous experience or formal qualifications will mean that new employees do not need training. (You are advised to keep a training record for each staff member so that it is clear what training they have received and, therefore, which duties they can be expected to perform.)

92 *On-the-job* training needs to be carried out under the guidance of an experienced operator/maintenance engineer who is familiar with the process, with emphasis being placed on safety precautions and methods of dealing with emergencies. Particular attention should be given to the following aspects:

- the hazards and characteristics of chlorine;
- safe methods of plant operation, including handling of cylinders or drums, connection to and disconnection from supply systems, together with regular monitoring and verification of the adequacy of the systems adopted;
- methods of maintenance and inspection, in particular the application of relevant standards and codes (see also paragraphs 84-87).
- special operations; for example, plant shut-down and start-up, methods of isolation<sup>47</sup> and preparation of equipment for periodic maintenance and inspection;
- the location and operation of emergency shut-off valves, ventilation equipment, alarms, leak detectors etc;
- the procedures to be followed if a release occurs; these should include isolation and containment of the release, and emergency plans. The procedures will need to be site specific and cover different scales of release (see also

paragraphs 106-118); and

training in the use of all personal protective equipment (PPE) supplied (see paragraph 96).

Maintenance staff should also cover defect rectification.

#### **Competency and audit**

93 Competence in the above topics needs to be assessed through post-training assessments using documented procedures. It is recommended that training and safety procedures are audited annually by management or an audit team with relevant experience as part of your company's audit programme. Internal audits may be supplemented by external audits from chlorine suppliers under the CIA's initiative for Responsible Care and Product Stewardship, or by other competent people at intervals of approximately three years for drum installations and five years for cylinder installations.

#### Personal protective equipment (PPE)

94 Chlorine is a highly toxic substance; acute exposure can be fatal (see Appendix 1). You therefore need to establish safe working practices and control measures (including PPE) and ensure that they are understood by operatives. Safe procedures are vital where it is necessary to enter an enclosed storage space or room where a chlorine leak has occurred. Work in such confined spaces is subject to The Confined Spaces Regulations 1997.<sup>48</sup> Guidance on how to comply with the Regulations is given in an Approved Code of Practice.<sup>49</sup> The precautions identified must be implemented and suitable training given to operators.

95 A common source of exposure to chlorine arises at operations involving the making and breaking of chlorine pipework connections, particularly to containers. Steps should be taken to prevent or, where that is not reasonably practicable, reduce personal exposure to chlorine<sup>20</sup> by means other than personal protective equipment. When personal protective equipment, including respiratory protective equipment, needs to be worn, equipment manufactured after 30 June 1995 should carry the CE mark to indicate that the equipment has been designed and tested to meet the basic requirements of Council Directive 89/686/EEC.

96 Respiratory protective equipment (RPE) that has been approved by HSE or is claimed by the manufacturer to conform to a standard approved by HSE, and which was manufactured before 1 July 1995, can continue to be used at work provided that it is still suitable and maintained in good condition. All personnel who are required to use RPE (for example, respirators, breathing apparatus (BA), or escape breathing apparatus) must receive adequate instruction and training in its safe and correct use. The RPE must be thoroughly examined and tested in accordance with the manufacturer's recommendations (typically at least once every month) and records kept.<sup>20</sup>

#### Selecting suitable respiratory protective equipment (RPE)

97 Where PPE including respiratory protective equipment (RPE) needs to be worn, you must ensure that it is properly selected and that it provides adequate protection.<sup>50,51</sup> When selecting RPE you should consult relevant guidance<sup>52,53</sup> and base your selection on the results of a risk assessment.<sup>20</sup> The selected RPE must:

- provide adequate protection for your particular circumstances (eg for specific tasks or for emergency escape); and
- be compatible with other demands of the job and the working environment.

The selected RPE should make the overall risk of injury while wearing RPE as low as reasonably practicable.

98 When selecting RPE for a particular application, a two-stage selection procedure is therefore recommended:

- Based on the results of your exposure risk assessment:
  - decide whether a respirator or BA, or either may be used; then
  - determine the minimum protection required from the RPE. This is done using the equation below. In deciding the maximum allowable concentration inside the facepiece you will need to take account of recognised exposure limits (see Appendix 1) or take account of your in-house limits.

Minimum Protection Required =	Workplace concentration outside the facepiece of the RPE
	Maximum allowable concentration inside
	the facepiece of the RPE

For emergency escape purposes where the exposure will be less than 15 minutes, the maximum allowable concentration in the above expression is the Short-Term Exposure Limit (STEL) (see Appendix 1). Now compare the Minimum Protection Required value with the Assigned Protection Factors (APF) indicated in HSG53<sup>53</sup> and identify a selection of equipment. (APFs shown in HSG53 have been published by the British Standards Institution).<sup>54</sup> These APF figures are a guide, not a hard and fast rule. Indeed, it should be recognised that protection levels below the APF are possible when RPE is *unsuitable* for the task and is *not* suited to the wearer and the environment. Where advice given in HSG53 is properly taken into account, it is possible to achieve protection at or above the published APF values. You may use higher APFs if you have good quality information (eg satisfactory face-fit results for those wearing RPE) to demonstrate that they apply in your workplace conditions and to the selected RPE. You can use the APF for the equipment selected to estimate the concentration inside the facepiece:

	Workplace concentration outside the
Concentration inside the facepiece =	facepiece
	APF

(Note: 'Nominal Protection Factors' (NPF) values have been used in the past for identifying a selection of equipment. This procedure is no longer valid because workplace studies have shown that many wearers may not achieve the level of protection indicated by NPFs.)

The next stage is to take account of the factors detailed in paragraphs 36-47 of HSG53 to help narrow down the choice. Always involve the wearers in the selection process, and where possible provide them with a choice of suitable RPE. This will help to ensure that it is suited to them individually, and increase the chances that it will be accepted and worn correctly.

Where there is doubt about the choice, you need to confirm with the manufacturer or supplier that the chosen equipment is suitable for the task and the conditions in which it is to be used. They have duties under the Health and Safety at Work etc Act 1974 to provide information on the limitations and capabilities of their RPE.

99 At some chlorine installations it is common practice for personnel to carry half-mask respirators fitted with suitable filters (eg: type and class: B1; colour: grey) for protection against chlorine. The purpose of this type of respirator is to provide an immediate protection in the event of an incident involving low concentrations of chlorine gas so that the wearer can escape into fresh air. This type of half-mask

respirator has an APF = 10 (ie maximum allowable workplace concentration =  $10 \times \text{STEL} = 10 \text{ ppm}$ ).

100 A full face mask with cartridge or canister has an APF of 40. The use of this type of respirator would typically be in or very near the open air during the connecting up or disconnecting of containers or breaking into previously purged chlorine systems. The operating procedures specific to the site should state whether the respirator has to be worn for each operation, or be 'at the ready' to be put on in case of need. A respirator (eg a mask fitted with a filter or canister) is not suitable for use in atmospheres which are immediately dangerous to life or health. In other words, respirators are not suitable for operations where there is a potential for a significant release of chlorine gas. In these circumstances a suitable breathing apparatus should be worn.

101 Filters have a shelf-life specified by the manufacturers beyond which they should not be used. Once filter-canister seals have been broken, filter life will depend on usage, contaminant concentrations, breathing rate etc. Your risk assessment combined with information from the filter manufacturer will determine the useful life of respirator filters; your decisions need to be communicated to the wearers. Once unsealed, filters should not be stored for re-use, but they may be used over a number of consecutive days provided they have not been exposed to concentrations of chlorine similar to, or above, those they are provided for.

102 A negative pressure demand BA with full face mask has an APF of 40. For major leaks, a positive pressure demand type BA with full face mask (ie a self-contained BA) would be appropriate, provided the minimum protection required was consistent with the APF (2000) (see paragraph 111). A self-contained breathing apparatus (SCBA) should always be worn (possibly with a gas-tight chemical protective suit) when entering an enclosed space or chlorine room where a significant leak has been detected or suspected. This is because the chlorine detector may be some distance away from the source of the leak or pockets of 'trapped' gas which are not dispersed by the ventilation system. The concentration in such areas may be much higher than those detected by the alarm system.

103 In certain circumstances, compressed airline breathing apparatus (CABA) may be suitable. However, this restricts people's movements and the trailing hose can add to the risk in areas with obstructions. In such situations, a self-contained breathing apparatus may be appropriate.

104 For indoor installations with multi-stage alarms, the forced ventilation system will have been switched off on activation of the higher level alarm. People entering the area to identify and eliminate the source of the leak should wear suitable BA (see paragraphs 111-113). Nobody should work alone in these circumstances. Any back-up staff in attendance for emergency action should wear suitable breathing apparatus 'at the ready'.

105 Emergency escape breathing apparatus is not intended for use during normal work and therefore HSE do not recommend it for anything other than emergency escape use.

## **Emergency arrangements**

Note: Further guidance will be available when the COMAH Regulations come into force in February 1999.

106 You need to inform the appropriate fire authority and police force of the presence of chlorine at your site. You should also involve them and your chlorine supplier at an early stage when developing and updating your emergency plan and procedures. Your emergency arrangements should be based on a risk assessment and include procedures on how gas releases may be dealt with safely by site personnel and on whether to call for assistance from beyond the site.<sup>17,55,56,57</sup> Your risk assessment should also address fire safety of the process or installation and possible impacts from neighbouring sites. General fire precautions should comply with the requirements of the Fire Precautions (Workplace) Regulations 1997.<sup>21</sup>

107 Your emergency plan should cover the foreseeable range of chlorine releases for your site; a summary of some of the important elements of a plan for large (particularly CIMAH/COMAH) sites is given in Appendix 7. A copy of the plan should be made available to all personnel involved in its implementation. It is recommended that the plan includes the names or positions of the people who will sound the off-site alarm. This may be someone on-site, or it may under some circumstances be the responsibility of the first fire officer on the site in the event of an emergency. The plan should also include first aid (see Appendix 1) and evacuation arrangements both on-site and, if appropriate, off-site (see Appendix 7).

108 Each installation needs to have means of warning all workers that a gas release has occurred. A wind direction indicator, mounted in a highly visible location, needs to be provided to help personnel decide the best direction in which to escape. The appropriate action to be taken following a gas release warning should be defined in written instructions, and appropriate training given.

109 For minor gas releases, you may only need to plan simple actions. In other circumstances however, a further system of special warnings may be required, which initiates the emergency plan and, if necessary, the off-site emergency plan. Under 'Chlor-Aid', the chlorine producers and suppliers (see Appendix 4) collaborate in dealing with chlorine emergencies at installations throughout the UK. The first call for assistance should be to the emergency services for incident control and rescue, and then to 'Chlor-Aid', (via your supplier) who will offer advice on how to deal with the release. The arrangements are outlined in a booklet published by the CIA<sup>58</sup> under the chemical industry's Responsible Care initiative.

110 Regular practices of the emergency plan should be arranged. Some of these should involve the emergency services who will advise on a suitable frequency.

#### **Emergency equipment**

111 Your risk assessment should consider the extent, type, and location of the emergency equipment including the need for chemical protection suits which provide total encapsulation. These can be compressed airline-supplied full suits or full protective suits worn over self-contained breathing apparatus (SCBA). SCBA with full face mask conforming to BSEN 137 (SCBA)<sup>59</sup> or airline BA conforming to BSEN 139<sup>60</sup> has an APF of 2000 (but see paragraphs 97-103). Self-contained equipment will supply air for up to about 40 minutes (see manufacturer's details). A warning system alerts the operator to leave the contaminated area when the pressure in the air cylinders falls below a stipulated figure. Compressed airline breathing apparatus provides the same protection without a time limit, but does

restrict freedom of movement in search and rescue operation.

112 Emergency escape breathing apparatus should be CE marked and incorporate eye protection (eg in the form of a hood or full face mask). Suitable HSE approved escape equipment may also be used if it was manufactured before 30 June 1995. Such equipment is for escape only and not for use during routine work.

113 Emergency and rescue equipment should be available and readily accessible in all chlorine plant areas, and its location suitably marked (see also paragraph 29). Such equipment needs to be regularly inspected and maintained. An inventory of the equipment should be kept and attached to the plant operational and emergency procedures.

#### **Control of leakages**

114 For a severe leak, possibly arising from a failure of pipework, the chlorine building will provide some delay to the release of the gas to the open air, provided vents and apertures are closed or sealed. This will give more time for the technical staff and management to identify and deal with the source of the release. In dispersing the contained release from a chlorine room it is still essential to consider the off-site consequences and it may be necessary to sound the off-site alarm (when fitted) to alert people to go indoors and remain there. It is for the emergency services to consider clearing people from the area immediately downwind of the installation following such a release. A significant reduction in the release of chlorine from the building is only obtained if the leak is quickly controlled and the rate of air change in the chlorine room is low. The ventilation system should, therefore, be switched off (unless a scrubbing system is installed to remove chlorine from the exhaust gas (see paragraph 81) and all apertures need to be closed or sealed. Airbricks should be taped up or sealed in some other way.

115 Consideration should be given to using an additional sensor capable of measuring concentrations up to 500 ppm and giving a visual display outside the chlorine room and in the works control room. Such a display is useful for assessing the significance of the leak and whether it can be isolated safely. Once concentrations exceed 1000 ppm (this is about the threshold concentration for the cloud to be visible), personnel dealing with the release should take additional precautions and should withdraw to a safe area as soon as they are aware that they are breathing contaminated air.

116 After a leak or substantial release has been dealt with it will be necessary to ventilate the chlorine room thoroughly. Operators should not remove any RPE until they have removed clothing (which may be contaminated with chlorine) and are in a safe environment.

117 Materials and equipment including sand and plastic sheets, to contain spills of liquid chlorine, should be readily available. If the spill is indoors and contained by the use of sand or a bund, it will rapidly cover itself with a coating of slushy chlorine hydrate and a cold vapour layer. Application of foam would cause renewed evolution of vapour because of the heat supplied. Covering a stabilised spill with plastic sheets is often the best action. The need for foam and water sprays should be discussed with the chlorine supplier and the local fire authority, since the use of foam and water may in certain circumstances aggravate the problem. The fire authority may carry stocks of suitable foam, but the decision to use it should be taken in conjunction with the senior technical manager on site.

118 Water should never be added to a spillage of liquid chlorine or sprayed onto

leaking drums or cylinders. However, water hoses or fog sprays directed at a chlorine gas cloud can help dilute it as a result of the air entrainment generated by the jets of water.

# Appendix 1 Toxicological properties and first aid

#### Toxicity

1 Chlorine has a perceptible odour that can be detected by most people at a concentration of 0.3 ppm (v/v) and by some at concentrations as low as 0.02 ppm. The Occupational Exposure Standard (OES)<sup>61</sup> for exposure to chlorine is 0.5 ppm; this is a time-weighted average concentration over a period of 8 hours. The Short-Term Exposure Limit (STEL)<sup>61</sup> is 1 ppm; a time-weighted average over 15 minutes.

2 It produces clear sensory irritation at concentrations of 0.5-1 ppm and above.<sup>62</sup> Irritation of the mucous membranes of the eye and nose, and especially of the throat and lungs, is caused by exposure to chlorine at levels of around 1-15 ppm. In general, irritation becomes intolerable at concentrations of about 4 ppm.<sup>63</sup> Concentrations of 50 ppm or more are dangerous even for exposures of about 5-10 mins; they may cause inflammation of the lungs with accumulation of fluid. Occasionally the development of respiratory symptoms may be delayed for up to two days after exposure. However, there is no convincing evidence of serious long-term sequelae following recovery from a single exposure to chlorine.<sup>62</sup>

3 Exposure to 1000 ppm may be fatal after a few breaths.<sup>64</sup> Death results from lung damage. It can either occur rapidly (from within hours to a couple of days post-exposure), due to oedema and congestion, or it can be somewhat more delayed (several days) due to secondary pneumonia.

4 The harm from exposure to chlorine is proportional to the 'toxic load' defined as the product of the square of the concentration and exposure time. For risk assessment work, HSE uses a 'dangerous toxic load' <sup>65</sup> (DTL) of: DTL = 108 000 ppm<sup>2</sup>min which is potentially fatal to the most vulnerable members of the population. Thus exposures to 104 ppm for 10 minutes or 73 ppm for 20 minutes etc are potentially fatal; the chance of fatality depends on many factors.<sup>65</sup>

#### **First aid**

5 When liquid chlorine comes into contact with the skin or mucous membranes it can produce serious burns which need to be treated by a medically competent person. People who have inhaled chlorine gas should be moved as quickly as possible into 'fresh air', laid in a restful position with the head and chest raised, and kept warm. It is essential that qualified medical attention is obtained quickly, as serious symptoms may develop up to 48 hours later. Anyone who has been affected by chlorine gas should be examined locally by a medically competent person or sent to hospital by ambulance.

6 First-aid attendants should be aware of the dangers arising from gassing by chlorine. The following basic rules should be observed:

 if chlorine has affected the eyes, they should be irrigated with plenty of clean (preferably tap) water;

- contaminated clothing should be removed in a well-ventilated area and affected skin washed with plenty of water;
- mouth-to-mouth resuscitation should not be given if the patient is breathing, because there is a risk of the attendant being harmed. However, oxygen may be administered or resuscitation equipment used by suitably qualified personnel.

More comprehensive guidance is given elsewhere.<sup>66</sup>

# Appendix 2 Characteristics of chlorine

1 Chlorine is a greenish-yellow gas at ambient temperature and pressure. It is supplied commercially as a liquid under pressure.

2 Commercial liquid chlorine conforms to BS 3947:1976.<sup>67</sup> This Standard specifies a minimum limit for the chlorine content and maximum levels for water content and residue on evaporation; details of the methods of analysis for gaseous impurities (carbon dioxide, oxygen and nitrogen), water content, nitrogen trichloride, and residue on evaporation are also given.

3 Traces of dissolved gaseous impurities in chlorine are not normally significant for most applications; moisture content however is extremely important because of the corrosive nature of wet chlorine.

4 Trace residues which are left on evaporation, usually chlorinated organic products or ferric chloride, may lead to blockage of pipelines, valves or instruments. Nitrogen trichloride can be potentially dangerous<sup>68,69</sup> if the vaporisation process leads to its concentration in residues, but this is generally not considered to be a problem in drum and cylinder installations.

5 Physical properties

Atomic weight		35.46	
Molecular	weight	70.91	
Density	liquid	1561 kg/m³ at -35°C 1468 kg/m³ at 0°C 1410 kg/m³ at 20°C	
	gas	3.173 kg/m <sup>3</sup> at 0°C and 1 bar absolute (relative density 2.490 at 20°C relative to air)	
Boiling po Melting po Critical ter Critical pro Vapour pr Viscosity: 1 volume absolute	int at 1.0133 bar absolute bint mperature essure essure at 20°C liquid at 20°C of liquid chlorine = 463 volumes	-34.05°C -101.6°C 144°C 77.1 bars absolute 6.7 bars absolute 0.35 cp s of chlorine gas at 0°C and 1 bar	

1 kg of liquid chlorine = 0.319 m<sup>3</sup> of chlorine gas at 0°C and 1 bar absolute

The variation of the vapour pressure of liquid chlorine with temperature is given in Figure A2.1.

Thermal properties

Specific heat (liquid chlorine between 1°C and 27°C) 0.236 kcal/kg/°C

Specific heat (gas at constant pressure at 6.9 bars absolute or less and between 1°C and 27°C) 0.113 kcal/kg/°C

Ratio of specific heat at constant pressure to specific heat at constant volume 1.355

Latent heat of fusion	21.6 kcal/kg
Latent heat of vaporisation at 0°C	63.2 kcal/kg

Coefficient of cubic expansion (liquid chlorine at 20°C) 0.0021 per °C

This coefficient is sufficiently large to result in excessive pressure should liquid chlorine be trapped in pipework between two closed valves with no gas space.

Heat of reaction of chlorine gas with sodium hydroxide liquor 348 kcal/kg of chlorine.

6 While the above data give a general summary of the physical and thermal properties of chlorine, more detailed information is needed for use in plant design calculations.



Figure 1 Variation of chlorine vapour pressure with temperature

#### Solubility of chlorine in water

7 Chlorine dissolves slightly in water to give a solution which has oxidising, bleaching and germicidal properties. The solubility of chlorine in water increases with the partial pressure of the chlorine. The table below gives the solubility of chlorine in water at different temperatures for a total pressure of 1 bar absolute:

Temperature °C	10	15	20	25
grams of chlorine per litre of water	9.97	8.5	7.29	6.41

For a total pressure of 1 bar absolute, the partial pressure of chlorine reduces as the water temperature (and hence the partial pressure of water vapour) increases.

8 On cooling below 9.6°C, crystals of chlorine hydrate (Cl<sub>2</sub>.8H<sub>2</sub>0) are deposited. For this reason, wet chlorine in process must always be kept above this temperature to avoid the blockages which would otherwise occur as a result of the formation of solid chlorine hydrate.

9 A solution of chlorine in water forms hydrochloric acid and hypochlorous acid:

$$CI_2 + H_2O$$
 HCI + HOCI

#### **Chemical properties**

10 Dry chlorine at ambient temperatures reacts directly with many of the elements producing chlorides both of non-metals (eg sulphur or phosphorus) and of metals (eg iron in a finely divided form, aluminium or titanium). Dry chlorine at ambient temperature does not attack steel, copper or nickel, but these metals are attacked at higher temperatures. Steel combines with dry chlorine above 200°C and, since the reaction is exothermic, the rate of reaction may increase rapidly. Reaction with nickel does not take place until the temperature exceeds 500°C.

11 Traces of moisture in chlorine lead to rapid corrosion of steel, copper and nickel.

12 Titanium is resistant to wet chlorine between 15°C and 100°C but reacts violently with dry chlorine and should *not* be used; but see paragraph 18.

13 Chlorine dissolves in cool aqueous solutions of alkalis to produce solutions of hypochlorites; in hot or boiling aqueous alkalis, chlorates can be produced.

14 Chlorine reacts vigorously with many organic compounds including mineral oils and greases, producing chlorinated products. The mechanism is either direct addition to unsaturated bonds or substitution of hydrogen. In the latter case, hydrogen chloride is formed as a by-product.

15 Mixtures of chlorine and hydrogen are explosive over a large range of concentrations; the explosion may be initiated by a spark, by photochemical action or by a catalyst. Under certain conditions chlorine reacts with ammonia to produce nitrogen trichloride, which is spontaneously explosive. This is not a risk when testing for leaks with a bottle of ammonia.

#### Selection of materials of construction

16 The choice of appropriate materials of construction for chlorine systems is considered in detail elsewhere.<sup>70</sup> Your options should be selected only after a detailed survey of all possible variations in operating conditions, and your preferred option decided in consultation with your chlorine supplier.

17 A system constructed of steel, which is appropriate for dry chlorine, must itself be dried adequately before commissioning. This may be done by purging with dry air or inert gas until the exit purge has a dew point below -40°C. However, the upper operating temperature must be limited.

18 The use of titanium metal for wet chlorine is satisfactory,<sup>70</sup> provided that the moisture level is always kept high and that control is exercised over the upper and lower operating temperature limit. Maintenance and inspection procedures must include awareness of the possibility of crevice corrosion. However, where titanium is used in plants containing wet chlorine (gas or liquid) consideration should be given to the possibility of a fault condition giving rise to contact between titanium and dry chlorine gas or liquid. If such a fault could possibly arise it may be best to consider alternative construction materials.

19 Materials which are resistant to attack by both wet or dry gaseous chlorine at ambient temperatures include glass, stoneware, porcelain, tantalum, ebonite and certain plastics. The use of plastic materials with *liquid* chlorine is unsatisfactory.

#### Learning from incidents

20 An interesting selection of incidents, which illustrate some of the above hazards (including a nitrogen trichloride explosion, a titanium/chlorine fire and external corrosion) and the means for controlling them, is reviewed in GEST/AP1.<sup>71</sup>

## Appendix 3 Relevant legislation and HSE guidance

1 The basis of health and safety law in the UK is the Health and Safety at Work etc Act 1974. This sets out general duties which employers have towards employees and members of the public, and those that employees have to themselves and each other. These duties are qualified in the Act by the principle of 'so far as is reasonably practicable'; ie the extent of the measures taken to avoid or reduce a particular risk to health and safety needs to be balanced against the time, trouble, cost, and physical difficulty involved. This balancing process<sup>72</sup> is often referred to as making risks 'as low as is reasonably practicable' (ALARP).

2 In essence, what health and safety legislation requires is what good management and common sense would lead employers to do anyway: that is to look at what the risks are and take sensible measures to make them ALARP. This broad requirement is made explicit in the Management of Health and Safety at Work Regulations 1992<sup>18,19</sup> (referred to as the Management Regulations). Like the Act, these Regulations apply to every work activity. Other regulations are more specific, eg the Manual Handling Operations Regulations (MHO)<sup>44</sup> or the Control of Substances Hazardous to Health Regulations (COSHH).<sup>20</sup>

3 A full list<sup>3</sup> of current legislation, Approved Codes of Practice and some guidance is published annually. The list contains legislation, which, although in existence, is spent or has lapsed. A price list of all available HSE publications is published annually by HSE Books. Contact details are on the inside of the back cover.

4 A number of regulations (eg COSHH, MHO, PPE,<sup>51</sup> Management Regulations

etc) specifically require you to undertake a risk assessment. A leaflet<sup>73</sup> is available describing how these assessments are linked together and what the requirements are; however, it does not deal with highly specialised risks such as major hazards.

- 5 Under the basic legal requirements you must:
- have a written, up-to-date health and safety policy if you employ five or more people;
- carry out a risk assessment (and if you employ five or more people, record the main findings and your arrangements for health and safety);
- notify occupation of premises to your local inspector if you are a commercial or industrial business;
- display a current certificate as required by the Employers' Liability (Compulsory Insurance) Act 1969 if you employ anyone;
- display the Health and Safety Law poster for employees or give out the leaflet;<sup>74</sup>
- notify certain types of injuries, occupational diseases and events (see paragraph 23); and
- consult employees and any appointed union safety representatives<sup>75</sup> on certain issues, such as any changes which might affect health and safety and any information, instruction and training which has to be provided.

6 The ALARP principle and the need for risk assessment enables the Health and Safety Commission, where appropriate, to make Regulations in a goal-setting form: ie setting out what must be achieved, but not how it must be done. Sometimes it is necessary to prescribe in detail what must be done and set absolute standards.

7 Some activities or substances are so inherently hazardous that they require additional arrangements. For example, chlorine installations which store 10 tonnes or more need to meet the general requirements of the CIMAH Regulations (see paragraph 9).

### The Notification of Installations Handling Hazardous Substances (NIHHS) Regulations 1982<sup>4</sup>

8 These Regulations implement a notification scheme for installations with inventories greater or equal to specified quantities (10 tonnes for chlorine). Notification is to the Health and Safety Executive via your Local Area Office (see Appendix 4). Under NIHHS the following requirements apply:

- before chlorine is used or stored at a site, at least three months notice must be given to HSE and certain details specified;
- the notification must be updated whenever there is a change in activity on site or there is an increase or reduction in the operational quantity of chlorine on site; and
- the amount of chlorine on site must not be increased to three or more times the quantity originally notified, unless a new notification is made. (Any increases in inventory levels must of course comply with other legislation, in particular section 3 of the HSW Act, ie that the risks to people off-site are ALARP).

#### The Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984<sup>5</sup>

9 These Regulations implement the requirements of the European Directive (82/501/EEC) on the major hazards of certain industrial activities commonly referred to as the 'Seveso' Directive. They apply to the storage and processing

of hazardous substances. The Regulations have been amended a number of times.<sup>3</sup> These include the 1988 amendment (revision of threshold quantities for certain substances) and the 1990 modification of the controls on storage following a serious warehouse fire. Two levels of activity are defined. The lower level requirements require companies to take the precautions that are necessary to prevent a major accident and to limit the consequences, and generally to demonstrate safe operation (regulation 4), and to report any major accident (regulation 5). Installations in which chlorine is involved in a process under Schedule 4 are subject to these general requirements regardless of the quantity present. unless the operation is incapable of producing a major accident hazard. Larger (ie top-tier) installations which store 75 or more tonnes, or installations with 25 tonnes or more which carry out process activities under Schedule 4, additionally require the preparation of safety reports, emergency plans and the provision of information to the public (regulations 7-13). Guidance on the CIMAH Regulations is available.56,76 These Regulations will be withdrawn when the proposed Control of Major Accident Hazards (COMAH) Regulations are implemented in February 1999.

#### The COMAH Regulations

10 These Regulations will implement the requirements of The Control of Major Accident Hazards Involving Dangerous Substances Directive (96/82/EC) which was adopted by the EU on 9 December 1996. The Directive is referred to as the 'Seveso II' Directive. The Regulations follow the Directive closely and mirror the Seveso I/CIMAH regime, in having two levels of duties:

- general duties on all operators subject to the Regulations: to notify the competent authorities of their activities, to take all measures necessary for the prevention and mitigation of major accidents, to prepare a major accident prevention policy, and report major accidents;
- top-tier duties on operators of sites where the quantities of dangerous substances exceed the higher thresholds. These operators must, in addition to the duties in the above paragraph, submit safety reports, prepare and test emergency plans and provide information to the public.

In the case of chlorine the threshold quantities are 10 tonnes for the general duties and 25 tonnes for the top-tier duties. Application depends solely on the presence or anticipated presence of the threshold quantities of dangerous substances, including dangerous substances which might be generated in the course of an accident due to loss of control of an industrial chemical process, with no differentiation between storage and processing. The general duty for operators to take 'all measures necessary for the prevention and mitigation of major accidents' is similar to the CIMAH Regulations which require manufacturers to 'take adequate steps to prevent ... major accidents ... and limit their consequences ...'. In judging how this duty should be complied with in practice, the competent authorities will base their view on whether risks have been reduced to ALARP. The main new requirements are:

- All operators within the scope of the Directive must produce a major-accident prevention policy (MAPP) and ensure that it is properly implemented to guarantee a high level of protection for humans and the environment by appropriate means, structures, and management systems.
- Land-use planning is brought within the scope of the Directive.
- Safety reports (top-tier sites only) have to be made available to the public, but companies can request that certain information, including commercial and personal confidential information, is withheld.
- The competent authorities, HSE and the Environmental Agency (EA) in England and Wales, and HSE and the Scottish Environmental Protection Agency (SEPA)

in Scotland, must prohibit operations where the measures taken by operators to prevent and mitigate major accidents are seriously deficient.

The Seveso II requirements place much more emphasis on the management of safety and the role of the safety report than in the original Seveso Directive (implemented by the CIMAH Regulations). Paragraphs 11-23 summarise the main requirements of other legislation that is relevant to the control of risks posed by installations handling chlorine.

### The Planning (Hazardous Substances) Act 1990 and Planning (Hazardous Substances) Regulations 1992<sup>7</sup>

11 The Act and Regulations introduce planning controls which are designed to ensure that hazardous substances can be kept or used in significant amounts only after the responsible authorities have had the opportunity to assess the degree of risk to people in the surrounding area and are satisfied that the risks are tolerable. In essence the Act and Regulations require sites to apply for 'hazardous substances consent' for inventory levels at or above specific amounts known as the 'controlled quantity' - 10 tonnes in the case of chlorine. Neighbouring sites within 500 m, and controlled by the same person, must be taken into account when deciding the maximum inventory. New sites must obtain hazardous substances consent at an early stage in the life cycle.

12 In England and Wales the controls are enforced by the Hazardous Substances Authority (HSA), usually the District or London Borough Council for the land in question, ie the Local Planning Authority (LPA). In Scotland the equivalent regulations are The Town and Country Planning (Hazardous Substances) (Scotland) Regulations 1993. They are enforced by the Scottish Office, Environment Department (SOED). HSE is a statutory consultee under the Act and advises HSAs and SOED on the nature and severity of the residual risk. The Act recognises that safety must be an overriding control. The controls apply, regardless of whether planning permission is required under other legislation.

13 Guidance on applying for hazardous substances consent in England and Wales is given in *Hazardous Substances Consent: Guidance for Industry* (produced by the Department of the Environment and the Welsh Office, 92 PLAN0001). SOED has issued circular 16/1993 *Hazardous Substances Consent: Guidance for Industry*.

#### The Dangerous Substances (Notification and Marking of Sites) Regulations 1990<sup>28,29</sup>

14 Where more than 25 tonnes of dangerous substances are present on a site (including chlorine) notification must be made to the fire authority and appropriate signs placed at site access points. The enforcing authority is the fire authority except in specified circumstances when it is HSE. The Regulations require all signs to conform to BS5378<sup>32</sup> and to be kept clean and free from obstructions.

#### The Management of Health and Safety at Work Regulations 1992<sup>18</sup>

15 These Regulations implement Council Directives 89/391/EEC (OJ No L183, 29.6.89, p1) and 91/383/EEC (OJ No L206, 29.7.91, p19) on the introduction of measures to encourage improvements in safety and health of workers at work. Under the Regulations you must:

assess the risks to the health and safety of your employees and non-employees

arising in, or from, your activities and review the assessment when there is significant change. Records of significant findings of the assessment must be kept where there are five or more employees;

- plan, organise, control, monitor and review the preventative and protective measures taken as a result of the assessment;
- appoint any competent person(s) needed to help you comply with legal obligations, for example, when having pressure systems examined;
- set out what should be done in case of serious and imminent danger at your premises, such as the spillage of an appreciable amount of chlorine;
- tell employees about the risks and precautions involved in their work; and
- provide health surveillance where necessary.

### The Lifting Plant and Equipment (Records of Test and Examinations etc) Regulations 1992<sup>77,78</sup>

16 You must:

- have certificates of test and examination (normally provided by manufacturers and suppliers) specifying safe working loads before first using chains, ropes and lifting tackle;
- have chains, ropes, lifting tackle, hoists and lifts thoroughly examined every six months by a competent person (often employed by an insurance company) and obtain and keep the report;
- ensure tests and thorough examinations of cranes are carried out before they are first used and obtain a certificate of test and examination specifying safe working loads. Periodic thorough examinations at least every 12 months are also required, for which a report should be obtained and kept.

HSE guidance is available.78

**Note:** These Regulations will be revoked and replaced in December 1998 by the Lifting Operations and Lifting Equipment (LOLER) Regulations (SI 1998/2307). Guidance will be published in an Approved Code of Practice on Safe Use of Lifting Equipment. The Provision and Use of Work Equipment Regulations 1998 (see paragraph 19) also apply to lifting equipment.

#### The Manual Handling Operations Regulations 199244

17 These Regulations implement the substantive provisions of Council Directive 90/269/EEC (OJ No L156, 21.6.90, p9) on the health and safety requirements for the manual handling of loads where there is a risk of back injury to workers. Employers must:

- avoid the need for hazardous manual lifting and handling if reasonably practicable;
- assess the risk of injury from any hazardous manual lifting and handling which cannot be avoided; and
- reduce the risk of injury accordingly.

Employees must:

- follow safe systems of work laid down by their employers;
- use mechanical aids provided by their employers properly; and
- remember to use the training provided on lifting.

#### The Control of Substances Hazardous to Health Regulations 1994<sup>20</sup>

18 These regulations re-enact, with minor modifications, the COSHH Regulations 1988 (SI 1988/1657). They impose requirements on employers using substances hazardous to health to protect employees and other people who may be exposed to such substances. They also impose certain duties on employees concerning their own protection from exposure.

Employers must:

- assess risks to health;
- prevent exposure;
- where prevention is not reasonably practicable, control exposure by, for example, isolating or enclosing the process or, if this is not reasonably practicable, local exhaust ventilation;
- maintain control measures in efficient working order and ensure that a thorough test and examination of engineering controls are carried out at suitable intervals. Records of such maintenance must be kept for at least five years;
- where prevention or control is insufficient on its own, provide personal protective equipment and maintain it;
- inform, instruct and train employees; and
- carry out air monitoring and health surveillance where necessary.

### The provision and Use of Work Equipment Regulations (PUWER) 1992<sup>42,43</sup>

19 These Regulations impose health and safety requirements with respect to the provision and use of work equipment (machinery, appliances, tools etc). They impose requirements upon employers, including the need to:

- provide work equipment that is suitable for the purpose for which it is used or supplied;
- take steps to ensure that the equipment is not used under conditions for which it is not suitable;
- maintain work equipment in an efficient working order and good repair and that any maintenance log is kept up to date;
- provide people who use work equipment with:
  - clear health and safety information and, where appropriate, written instructions; and
  - adequate training, including the risks involved and the precautions to be taken. (This also applies to supervisors and managers of such people.)
- protect people from dangerous parts of machinery by suitable protection devices;
- provide suitable and sufficient lighting at any place where a person uses work equipment;
- ensure that work equipment is marked in a clear and visible manner with appropriate health and safety information and warnings; and
- ensure that any warning device is unambiguous and easily perceived and understood.

*Note:* These Regulations will be revoked and re-enacted in December 1998. The new PUWER Regulations (SI 1998/2306) include new provisions for mobile work equipment.

#### The Confined Spaces Regulations 199748,49

20 These Regulations apply when it is necessary for workers to carry out work in a confined space including a chamber, tank, flue or a similar space, which, by virtue of its enclosed nature, gives rise to a 'foreseeable specified risk'. In the case of chlorine installations the most likely foreseeable specified risk is 'the loss of consciousness or asphyxiation of any person at work arising from gas, fume vapour or the lack of oxygen'. The Regulations prohibit the entry into a confined space for the purpose of carrying out work where it is reasonably practicable to carry out the work by other means. In other situations (for example, the isolation of a leak in a chlorine room) they impose requirements on employers including the need to:

- establish safe systems of work for entry to, or carrying out work in, or leaving a confined space that renders the activities safe and without risks to health;
- establish suitable and sufficient arrangements for the rescue of people in the confined space in the event of an emergency;
- ensure compliance, so far as is reasonably practicable, with the provisions of the Regulations in respect of any work carried out by employees, or other people - in which case the matters need to be within the employer's control.

#### The Pressure System and Transportable Gas Containers Regulations 1989<sup>25,26,27</sup>

21 These Regulations impose requirements for pressure systems containing a gas or liquefied gas at a pressure greater than 0.5 bar above atmospheric pressure. They impose requirements on designers, suppliers of pressure systems and on employers of people who modify or repair such systems. The intention of the Regulations is to prevent the risk of serious injury from stored energy as a result of the failure of a pressure system or part of it. A measure of the stored energy is given by multiplying the system pressure (bar gauge) and volume (litres). A pressure system is:

- a system comprising one or more pressure vessels of rigid construction, any associated pipework and protective devices (systems with a stored energy of 250 bar litre or less are exempt from some requirements, eg the written scheme of examination);
- the pipework with its protective devices to which a transportable gas container is, or is intended to be, connected; or
- a pipeline and its protective devices.

The transportable gas container is not part of the system. Employers must ensure that:

- all plant and systems are designed, constructed and installed to prevent danger;
- systems are properly maintained;
- modifications or repairs do not cause danger;
- there is a written scheme of examination41 of certain pressure vessels, such as chlorine vaporisers, fittings and pipework, drawn up by a competent person;
- examinations as set out in the written scheme are carried out by a competent person; and
- records are kept.

**Note:** The transportable gas container (TGC) part of these Regulations was revoked in 1996 and incorporated into The Carriage of Dangerous Goods (Classification, Packaging and Labelling) and Use of Transportable Pressure Receptacles Regulations 1996. These PSTGC Regulations will be replaced in November 1999 by The Pressure Equipment Regulations and The Pressure Systems Safety Regulations.

#### The Personal Protective Equipment at Work Regulations 1992<sup>50,51</sup>

22 These Regulations impose health and safety requirements when providing PPE and using it to protect people in the workplace. Employers must:

- provide suitable PPE free of charge to protect employees against risks which have not been controlled by other means;
- take all reasonable steps to ensure it is properly used;
- before providing PPE, assess risks to health and safety which have not been avoided by other means and define the characteristics required by PPE to make the risks ALARP; then select suitable PPE by matching those characteristics with those of PPE available;
- maintain the PPE provided in clean and efficient working order and provide suitable storage for it when not in use; and
- give information, instruction and training.

Employees must:

- use PPE provided; and
- report any loss or obvious defect to the employer.

#### The Reporting of Injuries, Diseases and Dangerous Occurrences Regulations (RIDDOR) 1995<sup>79, 80, 81</sup>

23 These apply to all employers and self-employed people and cover everyone at work. The main points are that you must:

- notify your inspector immediately, normally by telephone, if anybody dies, receives a major injury or is seriously affected by, for example, an electric shock or poisoning;
- notify your inspector immediately if there is a dangerous occurrence, eg a fire or explosion, which stops work for more than 24 hours;
- confirm telephone notifications in writing within ten days on F2508;
- report within seven days (on form F2508) injuries which keep an employee off work or unable to do their normal job for more than three days;
- report certain diseases suffered by workers on form F2508A; and
- keep details of reported incidents.

#### **Enforcing the law**

Health and safety laws relating to your firm will usually be enforced by a health and safety inspector from HSE. In some cases, eg a public swimming pool, health and safety law is enforced by the local authority.

25 Inspectors may visit workplaces without notice but you are entitled to see their identification before they come in. They may want to investigate an accident or complaint, or inspect safety, health and welfare at your premises. They have the right to talk to employees and safety representatives, take photographs and samples, and even in certain cases to impound dangerous equipment. They are entitled to co-operation and answers to questions.

26 Inspectors will be aware of the main risks in handling chlorine and will give you help and advice on how to comply with the law. If there is a problem, they may issue a formal notice requiring improvements or, where serious danger exists, one which prohibits the use of a process or equipment. Inspectors have powers to prosecute a firm (or an individual) for breaking health and safety law.

## Appendix 4 Useful contacts and standards

#### Chlorine producers and suppliers

Hays Process Chemicals Sandbach, Cheshire CW11 3PZ

Imperial Chemical Industries plc, Chlor Chemicals PO Box 13, The Heath, Runcorn, Cheshire WA7 4QF

Rhodia Ltd Staveley, Chesterfield S43 2PB

The Associated Octel Co Ltd PO Box 17, Ellesmere Port, Wirral, Cheshire L65 4HF

**BOC Ltd Special Gases** 24 Deer Park Road, London SW19 3UF (Note: BOC supplies only cylinders.)

Air Products (GB) Ltd Speciality Gases Department, Weston Road, Crewe CW1 1DF (*Note: Air Products supplies only drums and cylinders.*)

#### Other useful contacts

Chemical Industries Association (CIA) Kings Buildings, Smith Square, London SW1P 3JJ Tel: 0171 834 3399

The CIA runs a chlorine committee dealing with technical and liaison issues.

Water Services Association of England and Wales 1 Queen Anne's Gate, London SW1H 9BT Tel: 0171 957 4567; Fax: 0171 957 4666

#### HSE

You can find details of your local HSE office in your local telephone directory or the current edition of HSE35 *The Health and Safety Executive: Working with employers*, available from HSE Books.

You can find details of HSE Books and HSE's enquiry service on the inside back cover of this booklet.

Chlorine Institute Inc. 2001 L Street, NW, Washington DC 20036 USA

**Euro Chlor** Avenue E Van Nieuwenhuyse 4, Box 2, B-1160 Brussels, Belgium Tel: +32 2 676 72 11; Fax: +32 2 676 72 41

Euro Chlor publishes a wide range of relevant reports.<sup>22</sup> The new series (AP) of pamphlets on *learning from accidents* is essential reading (eg see reference 71).

UK suppliers of Euro Chlor approved globe valves

Descote Ltd 19 Sandy Lane, Weston Point, Runcorn, Cheshire WA7 4EX Tel: 01928 565666; Fax: 01928 565646

Shaw, Son & Greenhalgh Ltd Albert Street, Lockwood, Huddersfield HD1 3QG Tel: 01484 532425; Fax: 01484 512426

HSE priced and free publications can be viewed online or ordered from www.hse.gov.uk or contact HSE Books, PO Box 1999, Sudbury, Suffolk CO10 2WA Tel: 01787 881165 Fax: 01787 313995. HSE priced publications are also available from bookshops.

#### **British Standards Institute**

BSI Sales and Customer Services, 389 Chiswick High Road, London W4 4AL Tel: 0181 996 7000; Fax: 0181 996 7001

British Standards are available from the above address.

#### Standards relevant to chlorine

Specification for pipe threads for tubes and fittings where pressure-tight joints are made on the threads (metric dimensions) BS 21:1985

Specification for liquid chlorine BS 3947:1976 (1997)

Specification for filling ratios and developed pressures for liquefiable and permanent gases BS 5355:1976

Specification for unfired fusion welded pressure vessels BS 5500:1997

Specification for flat products made of steels for pressure purposes BS EN 10028: Parts 1, 2, 3:1993 and 4:1995

Specification for tolerances on dimensions, shape and mass for hot rolled steel plates 3 mm thick or above BS EN 10029:1991

Circular flanges for pipes, valves and fittings. Part 3: Section 3.1 Specification for steel flanges. Part 3 Section 3.3 Specification for copper alloy and composite flanges BS 1560: Part 3: 1989

Specification for bolting for flanges and pressure containing purposes BS 4882: 1990

Specification for compressed asbestos fibre jointing BS 1832:1991 (1997) Specification for bursting discs and bursting disc devices BS 2915: 1990

Transportable gas containers. Part 1 Specification for seamless steel gas containers above 0.5 litre water capacity BS 5045: Part 1 1982; Part 2 Specification for steel containers of 0.5 L up to 450 L water capacity with welded seams BS 5045: Part 2 1989

Specification for filling ratios and developed pressures for liquefiable and permanent gases BS 5355: 1976

Safety signs and colours. Part 1 Specification for colour and design BS 5378: Part 1 1980 (1995); Part 3 Specification for additional signs to those given in BS 5378: Part 1 BS 5378: Part 3 1982 (1995)

Polytetrafluoroethylene (PFTE) materials and products. Specification for fabricated unfilled polytetrafluoroethylene products BS 6564: Part 2 1991 (1996)

Specification for identification of pipelines and services BS 1710: 1984 (1991)

Schedule of paint colours for building purposes BS 4800: 1989 (1994)

Guide to implementing an effective respiratory protective device programme BS 4275: 1997

Specification for respiratory protective devices: self-contained open-circuit compressed air breathing apparatus BS EN 137: 1993

Respiratory protective devices: compressed airline breathing apparatus for use with a full face mask, half mask, or mouthpiece assembly. Requirements, testing, marking BS EN 139: 1995

Steels for pressure purposes. Part 3 Specification for corrosion and heat-resisting steels: plates, sheet and strip BS 1501: Part 3 1990

Specification for steels for fired and unfired pressure vessels: sections and bars BS 1502: 1982 (1990)

British Standards can be obtained in PDF or hard copy formats from the BSI online shop: www.bsigroup.com/Shop or by contacting BSI Customer Services for hard copies only Tel: 020 8996 9001 e-mail: cservices@bsigroup.com.

## Appendix 5 Outside installations and inside installations

1 Drum and cylinder installations should preferably be located in a building, but drums and cylinders may be off-loaded in the open air.

2 If the installation is located in the open air, canopy-type weather protection is recommended.

3 The advantages, disadvantages and consequent requirements of outside or inside installations are listed below.

#### **Inside installations**

- 4 The advantages of inside installations are that:
- valves and other equipment are protected from rain and snow, and provided the building is kept dry, there will be less risk of corrosion;
- background heating is possible, to help provide dry surroundings and increased chlorine vapour pressure for processes where inert gas/air padding is not acceptable;
- controlled ventilation is possible, limiting the external effects if the leak is fairly small;
- there is greater likelihood of a monitoring device detecting a leak; this is a particular advantage on an unattended plant; and
- the installation is protected from accidental mechanical damage, explosion or fire in adjacent plant or interference by unauthorised persons.

- 5 The disadvantages of inside installations are that:
- following a medium or major leak, emergency access may have to be made to a closed room with a high chlorine concentration;
- the point of leakage may be difficult to identify, owing to lack of dispersion, and mist formation;
- if the building is heated, there will be greater ground evaporation and flash from a liquid leak; and
- access for maintenance is likely to be more difficult.
- 6 It follows that indoor installations require:
- adequate forced ventilation systems, including start-up from operating points outside as well as inside the building; and
- careful consideration of plant layout and provision of adequate escape routes and escape respiratory equipment.

#### **Outside installations**

- 7 The advantages of outside installations are that:
- leakages are not confined, so the source of leakage is more safely accessible from upwind;
- it is easier to identify the point of leakage and take immediate local corrective action;
- access for installation and for major maintenance is simpler; and
- building costs are lower.
- 8 The disadvantages of outside installations are that:
- leakages may be detected at an early stage only from downwind positions;
- small leakages, particularly those arising from corrosion, can develop unnoticed;
- maintenance and repair work may have to be carried out in adverse weather conditions;
- there is no containment to reduce the rate of release to the atmosphere;
- surface corrosion is more likely; any leak may rapidly escalate; and
- there is less security.
- 9 It follows that outdoor installations require:
- strict vigilance and protection against corrosion;
- protection against possible mechanical damage and unauthorised access;
- an appropriate emergency system, possibly including procedures for the use of water sprays for gas clouds (see also main text paragraphs 106-118);
- weather protection for maintenance in critical areas; this could be either a permanent canopy or temporary sheeting; and
- continuous staffing on the site if a chlorine release could present serious consequences on or off site.

## **Appendix 6 Types of vaporiser**

Chlorine vaporisers may be divided into four basic types:

- Vertical tube bundle.
- Coiled tube immersed in a heating bath.
- Concentric tube.
- Kettle-type evaporator.

#### Vertical tube bundle (Type 1)







Advantages of this type of system are:

- small overall size for relatively large heat transfer surfaces;
- easy maintenance; and
- for the mode of operation in which the chlorine is in tubes, the liquid chlorine is automatically displaced by over-pressure when the vapour supply to the consuming plant is shut off.

Disadvantages of this type of system are:

- for the mode of operation in which the chlorine is in the tubes, there is a risk of instability at high throughput owing to variation of liquid levels and a possibility of corrosion in the region of the liquid surface; and
- for the mode of operation in which the chlorine is in the shell, it is difficult to dry out the shell.





Advantages of this type of vaporiser are:

- it is simple to maintain and operate;
- the long coil generally ensures adequate superheating;
- there are no problems with differential thermal expansion;
- plug flow operation avoids concentration of high boiling impurities;
- drying out of equipment before use is relatively easy; and
- liquid chlorine is automatically displaced when the vapour supply to the consuming plant is shut off.

Disadvantages of this type of vaporiser are:

- Iow throughput;
- external corrosion of the tube can easily occur, especially near the liquid surface;
- irregular internal erosion of the coil may occur; and
- internal inspection and cleaning of the coil is difficult.

#### Concentric tube units (Type 3)



Advantages of this type of system are:

- simple construction with minimum welding requirements;
- easy maintenance and operation;
- easy provision of adequate corrosion allowance;
- automatic displacement of liquid chlorine when the vapour supply to the consuming plant is shut off; and
- plug-flow operation above a certain minimum flow avoids concentration of high boiling impurities.

Disadvantages of this type of system are:

- potential instability of operation at high and low throughput;
- limitation of unit capacity owing to relatively small heat transfer surface area; and
- greater difficulty in obtaining adequate superheating of the chlorine.

#### Kettle-type evaporator (Type 4)



Advantages of this type of system are:

- it can be designed for large throughput;
- allowance for thermal expansion can easily be made; and
- operation is stable, provided that either the level of chlorine in the kettle or the pressure of chlorine fed to the vaporiser, is controlled.

Disadvantages of this type of system are:

- since the vessel contains a relatively large amount of liquid chlorine, leakage or excess pressure in the vessel pose a greater potential hazard;
- a relief system with a large capacity is required, unless the vaporiser is designed for high pressure;
- operation can result in concentration of nitrogen trichloride; the purging process required to reduce this hazard may be difficult to carry out on consumer premises;
- drying of the equipment on the chlorine side is difficult; and
- dismantling of the tubes is difficult and requires a large space.

## **Appendix 7 Emergency plans**

(**Note:** A fuller discussion of emergency plans appears in HSE's HSG25<sup>56</sup> and references 17, 57 and 58. Additional guidance will be issued to support the COMAH Regulations.)

1 The works should have an on-site emergency plan for dealing with a major chlorine release. The plan should include instructions for the emergency team and for non-essential personnel, and for liaison with the emergency services. The emergency plan should be based on paragraphs 106-118. Your plan will depend on the results of your risk assessment and the need to comply with health and safety legislation, eg section 3 of the HSW Act.<sup>2</sup> The following paragraphs contain some elements of a plan.

2 The plan may include detailed instructions for:

- raising the alarm;
- investigating and assessing the source and extent of the chlorine release;
- alerting all personnel on-site or in neighbouring premises and the emergency services; setting up emergency control centres, assessment by key personnel of the incident and consequent emergency measures on and off-site;
- methods for controlling the chlorine release;
- search systems for casualties, and accounting for personnel on-site;

- methods for assessing the directional spread and concentration of the gas cloud;
- criteria for determining whether to evacuate non-essential personnel or to advise them to stay inside buildings with doors, windows and ventilation shut;
- methods for assessing whether corresponding actions are advisable for people off-site and, in particular, liaison with the manager at any adjacent underground workings where chlorine could enter the ventilation system; advice to emergency services on the direction, spread and concentration of the gas cloud; and
- first aid to on-site casualties, and arrangements for evacuation where advisable and practicable; advice to ambulance service on routes to use.

3 Since each installation will have its own special features, a detailed plan relating to the particular plant will be required. Local management should be responsible for preparation of the plan which should be developed in co-operation with the local authority, the police, fire, hospital and ambulance services, and the chlorine supplier. Specific duties are laid on some of these people by the Control of Industrial Major Accident Hazards Regulations 1984. These will be superseded by the requirements of the COMAH Regulations in 1999.

#### **Emergency control centres**

4 Basic requirements for a satisfactory system to deal with an emergency resulting from a serious escape of chlorine are outlined as follows:

- two control centres should be provided so that, in the event of a gas escape, operations can be controlled from the centre which is least affected under prevailing atmospheric conditions;
- each centre should be provided with a separate external telephone line, as well as with connections to the factory's external and internal telephone system;
- adequate emergency equipment (self-contained breathing apparatus, supplies of suitable foam as agreed with the emergency services, protective clothing, etc) should be available (see section on emergency equipment);
- emergency first-aid facilities, including equipment for administering oxygen, need to be provided;
- a large-scale map (1:25 000 or 1:10 000) of the surrounding area should be available to help determine which parts of the factory and the local neighbourhood are likely to be affected;
- wind direction indicators have to be visible from, or indicated in, each control centre; and
- equipment and information are needed to assess the likely extent of the gas cloud for various sizes of release and various weather conditions.

5 The emergency plan should specify in advance the individuals and deputies responsible for the action necessary to deal with the emergency.

#### Site emergency team

- 6 There should be a trained emergency team with the following key personnel:
- Site incident controller the senior person on-site responsible for the direction of on-site operations;
- Site main controller normally the works manager or deputy with overall responsibility for the operation of the emergency plan, maintaining close liaison with the police and fire services, and for advising them on the risk; and

- Other key personnel including:
  - the team responsible for the control of the chlorine release;
  - the team responsible for the search for casualties, for first aid and for the control of evacuation.

7 The police will be responsible for dealing with members of the public who might be affected by the chlorine escape; they will need to be advised of the size and expected duration of the release together with the areas which could be affected, to allow the police and the site main controller to agree whether the public should remain indoors or be evacuated.

#### **Emergency assembly areas**

8 Emergency assembly areas should be designated for use in a chlorine emergency by personnel not involved in the emergency team. The assembly areas allow for counting of personnel and for controlled evacuation if the need should arise. Preferably, the assembly area should be at the periphery of the works site with good exit for evacuation. A building with upper storeys at a location upwind of the chlorine release may offer sufficient protection while the release is brought under control. Evacuation of personnel to the assembly areas should be directed by a senior member of the emergency team who will take wind direction into account. There will be occasions when evacuating off-site is not the best action, for example, when the release is sudden and of limited duration.

#### **Casualties**

9 First-aid treatment for casualties is discussed in Appendix 1.

### References

- 1 Safety advice for bulk chlorine installations HSG28 HSE Books 1999 ISBN 0 7176 1645 2
- 2 Health and Safety at Work etc Act 1974
- 3 List of current health and safety legislation 1996 HSE Books 1997 ISBN 0 7176 1311 9
- 4 The Notification of Installations Handling Hazardous Substances Regulations 1982 SI 1982/1357 HMSO
- 5 The Control of Industrial Major Accident Hazards Regulations 1984 SI 1984/1902 HMSO
- 6 Council Directive 96/82/EC Control of major-accident hazards involving dangerous substances Official J of the EC No L10/40 CEC January 1997
- 7 The Planning (Hazardous Substances) Regulations 1992 SI 1992/0656 HMSO
- 8 Risk criteria for land-use planning in the vicinity of major industrial hazards HSE Books 1989 ISBN 0 11 885491 7

- 9 Environmental Protection (Prescribed Processes and Substances) Regulations 1991 SI 1991/0472 HMSO
- 10 Environmental Protection Act 1990
- 11 Alkali and Works Regulation Act 1906
- 12 Health and Safety (Emissions into the Atmosphere) Regulations 1983 SI 1983/0943 HMSO
- 13 The Carriage of Dangerous Goods (Classification, Packaging and Labelling) and Use of Transportable Pressure Receptacles Regulations 1996 SI 1996/2092 HMSO
- 14 The Carriage of Dangerous Goods by Road Regulations 1996 SI 1996/2095 HMSO
- 15 Are you involved in the carriage of dangerous goods by road or rail? INDG234 HSE free leaflet 1996
- 16 Successful health and safety management HSG65 HSE Books 1997 ISBN 0 7176 1276 7
- 17 Formula for health and safety: guidance for small to medium-sized firms in the chemical manufacturing industry HSG166 HSE Books 1996 ISBN 0 7176 0996 0
- 18 The Management of Health and Safety at Work Regulations 1992 SI 1992/2051 HMSO
- 19 Management of health and safety at work. Approved Code of Practice. Management of Health and Safety at Work Regulations 1992 L21 HSE Books1992 ISBN 0 7176 0412 8
- 20 The Control of Substances Hazardous to Health Regulations 1994 SI 1994/3246 HMSO
- 21 The Fire Precautions (Workplace) Regulations 1997 SI 1997/1840 TSO
- 22 Publications: Literature and technical documentation Euro Chlor 1997\*
- 23 Transportable gas containers. Part 1 Specification for seamless steel gas containers above 0.5 litre water capacity BS 5045: Part 1 1982; Part 2 Specification for steel containers of 0.5 L up to 450 L water capacity with welded seams BS 5045: Part 2 1989
- 24 Specification for filling ratios and developed pressures for liquefiable and permanent gases BS 5355: 1976
- 25 The Pressure Systems and Transportable Gas Containers Regulations 1989 SI 1989/2169 HMSO
- 26 Safety of pressure systems. Pressure Systems and Transportable Gas Containers Regulations 1989. Approved Code of Practice COP 37 HSE Books 1990 ISBN 0 11 885514 X

- 27 A guide to the Pressure Systems and Transportable Gas Containers Regulations 1989 HSR30 HSE Books 1990 ISBN 0 7176 0489 6
- 28 The Dangerous Substances (Notification and Marking of Sites) Regulations 1990 SI 1990/0304 HMSO
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- 30 The Health and Safety (Safety Signs and Signals) Regulations 1996 SI 1996/ 0341 HMSO
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- 32 Safety signs and colours. Part 1 Specification for colour and design BS 5378: Part 1 1980 (1995); Part 3 Specification for additional signs to those given in BS 5378:Part 1 BS5378 Part 3 1982 (1995)
- 33 Process piping B31.3 American Society of Mechanical Engineers 1996
- 34 *Chemical plant and petroleum refinery piping* Supplement to B31.3 American Society of Mechanical Engineers 1995
- 35 Specification for pipe threads for tubes and fittings where pressure-tight joints are made on the threads (metric dimensions) BS 21:1985
- 36 Kletz TA Hazop and Hazan: Identifying and assessing process industry hazards 3rd ed IChemE 1992 ISBN 0 85295 285 6
- 37 Specification for compressed asbestos fibre jointing BS 1832: 1991 (1997)
- 38 Polytetrafluoroethylene (PTFE) materials and products. Part 2 Specification for fabricated unfilled polytetrafluoroethylene products BS 6564:Part 2 1991 (1996)
- 39 Specification for identification of pipelines and services BS 1710: 1984 (1991)
- 40 Schedule of paint colours for building purposes BS 4800: 1989 (1994)
- 41 Written schemes of examination. Pressure Systems and Transportable Gas Containers Regulations 1989 INDG178 HSE free leaflet 1994
- 42 The Provision and Use of Work Equipment Regulations 1992 SI 1992/2932 HMSO
- 43 Work equipment. Provision and Use of Work Equipment Regulations 1992. Guidance on Regulations L22 HSE Books 1992 ISBN 0 7176 0414 4
- 44 The Manual Handling Operations Regulations 1992 SI 1992/2793 HMSO
- 45 Manual handling. Manual Handling Operations Regulations 1992. Guidance on Regulations L23 HSE Books 1992 ISBN 0 7176 0411 X
- 46 Permit-to-work systems INDG98 (rev3) HSE free leaflet 1998

- 47 HSC Oil Industry Advisory Committee *The safe isolation of plant and equipment* HSE Books 1997 ISBN 0 7176 0871 9
- 48 The Confined Spaces Regulations 1997 SI 1997/1713 TSO
- 49 Safe work in confined spaces. Confined Spaces Regulations 1997 Approved Code of Practice and Guidance L101 HSE Books 1997 ISBN 0 7176 1405 0
- 50 The Personal Protective Equipment at Work Regulations 1992 SI 1992/2966 HMSO
- 51 Personal protective equipment at work. Personal Protective Equipment at Work Regulations 1992 Guidance on Regulations L25 HSE Books 1992 ISBN 0 7176 0415 2
- 52 GEST 92/171 1995 Personal protective equipment for use with chlorine Euro Chlor 1995\*
- 53 The selection, use and maintenance of respiratory protective equipment: A practical guide HSG53 HSE Books 1998 ISBN 0 7176 1537 5
- 54 Guide to implementing an effective respiratory protective device programme BS 4275:1997
- 55 Prepared for emergency INDG246 HSE free leaflet 1997
- 56 Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH): Further guidance on emergency plans HSG25 HMSO 1985 ISBN 0 11 883831 8
- 57 Robinson BW and UK Chlorine Producers General guidance on emergency planning within the CIMAH Regulations for chlorine installations 1986\*\*
- 58 Inter-company collaboration for chlorine emergencies CIA 1992 ISBN 0 900 623\*\*
- 59 Specification for respiratory protective devices: self-contained open-circuit compressed air breathing apparatus BS EN 137: 1993
- 60 Respiratory protective devices. Compressed airline breathing apparatus for use with a full face mask, half mask or mouthpiece assembly. Requirements, testing, marking BS EN 139: 1995
- 61 *Occupational exposure limits* EH40 /98 HSE Books (updated annually) ISBN 0 7176 1474 3
- 62 WHO International Programme on Chemical Safety *Environmental Health Criteria 21 Chlorine and hydrogen chloride* World Health Organisation, Geneva, 1982
- 63 Summary criteria for occupational exposure limits EH64 HSE Books (updated annually) ISBN 0 7176 1576 6
- 64 Lewis RJ Sax's dangerous properties of industrial materials (9th ed) Van Nostrand Rheinhold 1996 ISBN 0 4420 2025 2

- 65 Turner RM and Fairhurst S *Toxicology of substances in relation to major hazards: Chlorine* HSE Books 1990 ISBN 0 11 885528 X
- 66 GEST 89/145 Guidelines for medical management of chlorine exposure (3rd ed) 1995 Euro Chlor\*
- 67 Specification for liquid chlorine BS 3947: 1976 (1997)
- 68 GEST 76/55 Maximum levels of nitrogen trichloride in liquid chlorine 1990 Euro Chlor\*
- 69 Safe handling of chlorine containing nitrogen trichloride Chlorine Institute Pamphlet 152†
- 70 GEST 79/82 Choice of materials of construction for use in contact with chlorine (7th ed) 1995 Euro Chlor\*
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- 72 The setting of safety standards: A report by the Interdepartmental Group and external advisors 1996 HM Treasury<sup>††</sup>
- 73 A guide to risk assessment requirements: Common provisions in health and safety law INDG218 HSE free leaflet 1996
- 74 Health and Safety Law: What you should know (poster) HSE Books IBSN 0 7176 1380 1
- 75 The Health and Safety (Consultation with Employees) Regulations 1996 SI 1996/1513 HMSO
- 76 A guide to the Control of Industrial Major Accident Hazards Regulations 1984 HSR21(rev) HSE Books 1990 ISBN 0 11 885579 4
- 77 The Lifting Plant and Equipment (Records of Test and Examination etc) Regulations 1992 SI 1992 /0195 HMSO
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- 79 The Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1995 SI 1995/3163 HMSO
- 80 A guide to the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1995 L73 HSE Books 1996 ISBN 0 7176 1012 8
- 81 Everyone's guide to RIDDOR HSE31 HSE free leaflet 1996

The future availability and accuracy of the references listed in this publication cannot be guaranteed. Current Regulations, guidance and ACOPs are listed in the latest version of reference 3. Current HSE publications are listed in the latest version of HSE's list of priced publications which is published annually by HSE Books.

- \* Available from Euro Chlor, see address in Appendix 4.
- \*\* Available from CIA or chlorine producers, see addresses in Appendix 4.
- + Available from CIA, see address in Appendix 4.

Available from The Public Enquiry Unit, HM Treasury, Parliament Street, ++ London SW1P 3AG Tel: 0171 270 4558

For details on how to obtain HSE priced and free publications, see inside back cover.

## List of acronyms and abbreviations

ACOP	Approved Code of Practice
ALARP	As Low As Reasonably Practicable
ANSI	American National Standards Institute
APF	Assigned Protection Factor
ASME	American Society of Mechanical Engineering
BA	Breathing Apparatus
BS	British Standard
CABA	Compressed Airline Breathing Apparatus
CAF	Compressed Asbestos Fibre
CEC	Commission of the European Communities
CIA	Chemical Industries Association
CIMAH	Control of Industrial Major Accident Hazards (Regulations)
COMAH	Control of Major Accident Hazards (Regulations)
COSHH	Control of Substances Hazardous to Health (Regulations)
DTL	Dangerous Toxic Load
EA	Environment Agency
EEC	European Economic Community
EU	European Union
HAZOP	Hazard and Operability
HMSO	Her Majesty's Stationery Office
HSA	Hazardous Substances Authority
HSE	Health and Safety Executive
HSR	Health and Safety Regulations (Booklet)
HSW	Health and Safety at Work
LOLER	Lifting Operations and Lifting Equipment Regulations
LPA	Local Planning Authority
MHO	Manual Handling Operations (Regulations)
MHSW	Management of Health and Safety at Work (Regulations)
NIHHS	Notification of Installations Handling Hazardous Substances (Regulations)
OEL	Occupational Exposure Limit
OES	Occupational Exposure Standard
OJ	Official Journal (of the European Communities)
PPE	Personal Protective Equipment
ppm	Parts per million (by volume)
PSTGC	Pressure Systems and Transportable Gas Containers (Regulations)
PTFE	Polytetrafluoroethylene
PUWER	Provision and Use of Work Equipment Regulations
RIDDOR	Reporting of Injuries, Diseases and Dangerous Occurrence Regulations
RPE	Respiratory Protective Equipment
SCBA	Self Contained Breathing Apparatus
SEPA	Scottish Environmental Protection Agency
SI	Statutory Instrument
SOED	Scottish Office, Environment Department
STEL	Short-Term Exposure Limit

TGC	Transportable Gas Container
TSO	The Stationery Office
UK	United Kingdom
UPVC	Unplasticised Polyvinyl Chloride

WSE Written Scheme of Examination

#### **Further information**

For information about health and safety ring HSE's Infoline Tel: 0845 345 0055 Fax: 0845 408 9566 Textphone: 0845 408 9577 e-mail: hse.infoline@natbrit.com or write to HSE Information Services, Caerphilly Business Park, Caerphilly CF83 3GG.

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