

FIRE AND EXPLOSION HAZARDS OF CHLORINE-CONTAINING SYSTEMS

TJIBBE DOKTER*

Akzo Zout Chemie Ned. B.V., Research Group Explosion Safety and High Pressure Research, P.O. Box 25, 7550 GC Hengelo (The Netherlands)

(Received July 4, 1984; accepted in revised form September 10, 1984)

Summary

In the chemical industry chlorine is an important compound, produced and used on a very large scale. This paper deals with the fire and explosion hazards of chlorination reactions and the handling of free and bound chlorine-containing systems. Some relevant characteristics will be presented, such as flammability limits, auto-ignition, quenching diameter, burning velocity and detonation limits, especially for the system methyl chloride–chlorine. Autoignition temperatures of systems containing chlorine as an oxidant are usually much lower than the corresponding values in air or oxygen. For example, for methyl chloride the value measured (215°C) is approximately 400 degrees lower than the corresponding value in air. On the basis of the information available and a number of cases illustrating the field of interest, the general case of chlorine-containing systems will be discussed and some consideration given to the safe handling of these systems in a chemical plant, especially in the gas phase.

Introduction

Most organic gases and vapours do form explosive mixtures with chlorine. These mixtures can present an explosive hazard in many industrial installations. A rather extensive review of the explosion hazards of systems containing free and bound chlorine is presented in Ref. [1]. This paper provides some additional information, based mainly on our own experimental work as well as a number of accidents and near misses we have been faced with.

Although there is no theoretical difference between systems containing chlorine as an oxidant and oxygen-containing systems, there are some distinct practical differences. The most pronounced differences and their consequences for practical applications are:

Oxygen is a permanent gas at ambient temperatures and atmospheric pressure, while chlorine can easily be compressed to form a liquid at moderate pressures at ambient temperatures. In that case dissolution of organics in the liquid phase is possible, which changes the originally gaseous phase

*Present address: Methanor v.o.f., P.O. Box 109, 9930 AC Delfzijl, The Netherlands

explosion problem into a condensed phase problem with much higher potential for serious damage in the case of an explosion.

Chlorine is dissociated into radicals to a much higher degree than is oxygen at the same temperature. The radical level necessary to support a flame is reached at a much lower temperature, resulting in a much lower autoignition temperature. For the same reason chances of a thermal explosion are more serious at "normal" temperatures used in industrial practice (100–300°C).

Chlorine has a much higher density, thermal conductivity, specific heat and a lower velocity of sound than oxygen. The higher thermal conductivity causes a flame to move more easily through small holes. That means the quenching distance and the quenching diameter are markedly smaller than in oxygen systems. In general the burning velocities will be lower than in oxygen.

In chlorination proton abstraction is always the first step, and the hydrogen chloride formed behaves almost as an inert compound. In oxygen systems the formation of carbon–oxygen compounds is often an intermediate step. The proton abstraction possibility and the formation of the stable hydrogen chloride result in far more carbon formation in the post-flame zone.

Thermal explosions

The autoignition temperatures of a number of organics in chlorine are known and are much lower than the corresponding value in air or oxygen; sometimes they are below 150°C, but more often between 150 and 350°C (see Table 1). This means that when a mixture of a combustible and chlorine is formed at temperatures of 100°C and above, a serious thermal explosion hazard or ignition hazard is present when the mixture is allowed to reside for some time.

TABLE 1

Autoignition temperatures of a number of compounds in air (measured by the normalized technique) and in chlorine

Component	Air (°C)	Chlorine (°C)
H ₂	400	207
CH ₄	537	318 (<250?)
CH ₃ Cl	618	215 (<200?)
CH ₂ Cl ₂	556	262
C ₂ H ₆	472	205
C ₃ H ₆	455	150 (sooted surface 100–110)
1,2-C ₃ H ₆ Cl ₂	555	180

Sources: Refs. [2–4] and own data.

Explosive limits

For a number of organic compounds the explosive limits in chlorine are known (see Table 2). The limits in air and oxygen are given also. From this table it can be seen that in most cases the limits are comparable, especially on the rich side. No flammability data for alkenes and alkynes have been incorporated as in chlorine-containing systems the determination of explosion limits is meaningless because of the immediate addition reaction taking place upon mixing of the components.

TABLE 2

Explosion limits of several compounds in air, oxygen and chlorine

Component	Air (mol %)	Oxygen (mol %)	Chlorine (mol %)	Temperature (°C)
H ₂	4.0—75.6	3.9 —95.8	3.5 —89	
CH ₄	4.0—16.0	5.0 —61.85	5.51—63	
			3.6 —66	100
			0.6 —	200
CH ₃ Cl	7.0—17.4	8.05—66.0	10.2 —63.0	
CH ₂ Cl ₂	12 —22	12.65—73.4	16.5 —52.9	
CH ₃ OH	5.5—40		13.80—73.5	70
HCOOH			27.62—82.0	105
C ₂ H ₆	3.0—15.4	3.0 —67	4.95—58.8	
C ₂ H ₅ Cl	3.5—15.4	4.0 —67	8.98—49.2	
1,1-C ₂ H ₄ Cl ₂	5.3—	5.2 —63		
1,2-C ₂ H ₄ Cl ₂	4.5—17.3	4.0 —67.5	16.4 —36.8	100
C ₂ H ₅ OH	3.3—19		5.06—64.1	83
CH ₃ COOH	3.1—17	4 —60	15.83—56.0	122

The sources are Refs. [1—24]. There usually is some discrepancy in the values measured due to differences in experimental methods (Compare the catalytical method in Ref. [7], that will probably give too conservative figures.)

When the combustible (single component or mixture) is capable of exothermic decomposition into carbon and hydrogen chloride, the mixture or component is unstable and subject to more serious explosions or detonations than the components themselves (Hattwig [26]). In chlorine systems hydrogen chloride does not terminate the radical chain, so the inhibiting effect of this compound and that of chlorine itself that is sometimes observed in oxygen containing systems, is not present in chlorine systems. Due to the fission of hydrogen chloride from the molecule or the presence of hydrogen chloride in the mixture a slight widening of the explosion limits is sometimes observed, caused by the oxidative chlorination by the mixture of oxygen and hydrogen chloride [1].

Detonations

Chlorine is capable of forming detonable gaseous mixtures with a number of compounds. The best-known mixture is that with hydrogen, but methane [27] and methyl chloride also can detonate if mixed with the proper amount of chlorine. Bound chlorine-containing compounds do detonate also in many cases with oxygen or air; mixtures of trichloroethylene and oxygen, for instance, detonate very easily over a broad range of compositions (6.9% to 64.7%). Some data concerning the detonation limits are given in Table 3.

TABLE 3

Detonation limits for some compounds in air, oxygen and chlorine

Component	Air (mol %)	Oxygen (mol %)	Chlorine (mol %)
H ₂	18.2–58.9	9–95.3	17.5–83
CH ₄	6.3–13.5	6.7–56	15–45
CH ₃ Cl		10.5–63	12.5–55
CH ₂ Cl ₂	–17.3	11.5–75.8	

Sources: Refs. [20, 25–27] and own measurements.

Other aspects

Although the achievement of a spark in pure chlorine will require a much higher voltage due to the electronegativity of chlorine, spark ignition at normal pressures is quite easy [28]. The exact ignition energies are not known, but they seem to be quite low compared to oxygen-containing systems.

Methyl chloride—chlorine

In Ref. [23] the results of a study concerning the explosion limits of the system methyl chloride, methylene chloride, hydrogen chloride and chlorine is reported (see also Table 2). These results show that if the number of hydrogen and chlorine atoms in the mixture is equal, the explosion limits are widened and a large amount of carbon is formed due to an exothermic decomposition giving hydrogen chloride, as was also found by Hattwig [26].

An explanation of the irregular behaviour of the upper flammability limit of methyl chloride, hydrogen chloride and chlorine mixtures is the exothermic decomposition of methylene chloride even at relatively low temperatures, giving carbon and hydrogen chloride as products, thus causing a widening of the explosion limits.

The effect of carbon formation in systems where there is an excess of combustible (rich mixtures) is a general phenomenon. Large amounts of carbon

tetrachloride are also found, besides measurable quantities of tetrachloroethylene, hexachloroethane, chlorobutanes, chlorohexanes and chlorobenzenes. (These last three groups of compounds only in minor amounts, however.)

At the lower limit (surplus of chlorine), practically no carbon is formed and carbon tetrachloride together with perchloroethylene are the main products, besides hydrogen chloride.

The burning velocity of methyl chloride and chlorine can reach values above 36 cm/s, the value for methane—chlorine being approximately 70 cm/s [4]. For the quenching diameter of methyl chloride in chlorine a minimum value of 0.925 mm was found, which is low compared to the values found in oxygen-containing systems.

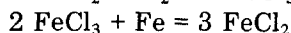
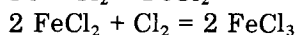
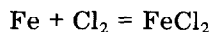
The detonation limits of methyl chloride and chlorine are 12.5% to 55% (hydrogen—oxygen predetonation was used as an ignition source). The maximum detonation velocity measured is 1135 m/s and the maximum stable detonation pressure measured is 26.9 bar, while in the transition area a pressure of 41.1 bar has been recorded (starting conditions: pressure 1 bar at ambient temperature).

Chemical considerations

Both chlorine and chlorinated hydrocarbons can be very reactive with their surroundings. Chlorine reacts with almost every material it comes in contact with, metals, organic material (including a number of polymers), chlorinated hydrocarbons and many inorganic compounds. A number of reactions are specially noteworthy:

Reaction of chlorine with metals

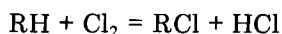
An example is the reaction of chlorine with iron:



The net result is that when the iron chlorides can dissolve either in chlorine (due to other components present), or in water, for example, the dissolution of the metal (corrosion) will be greatly enhanced. Under certain conditions, especially at higher temperatures, the iron chloride will evaporate (b.p. 315°C) and the reaction will proceed much faster, eventually resulting in an iron—chlorine fire at temperatures as low as 190°C with ordinary steel. Many other metals, too, are very reactive with chlorine (e.g., titanium, tin, aluminium) [11].

Reaction of chlorine with organic materials

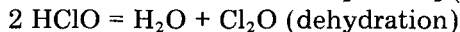
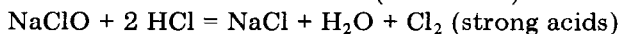
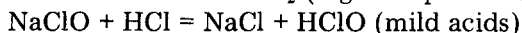
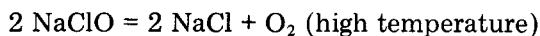
Chlorine reacts with almost every organic compound containing hydrogen and/or nitrogen. The simple chlorination reaction



takes place very easily and in many cases with a possibly explosive speed, even at relatively low temperatures or under the influence of light even at ambient temperatures. When both the combustible and the chlorine are in the liquid phase, the explosion can be much more serious than in the case of a gaseous system.

Organic nitrogen compounds generally form nitrogen trichloride [29] and some dinitrogenoxide, apart from large quantities of nitrogen. Nitrogen trichloride is a very unstable compound giving a detonation very easily, both in the gaseous and in the liquid phase.

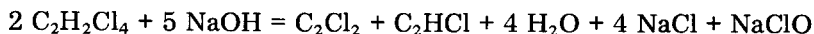
Many inorganic compounds also react with chlorine, especially amines, mainly entailing a danger of nitrogen trichloride formation. In the case that compounds containing both chlorine and oxygen are present, dichloromonoxide, chlorooxide and chlorodioxide may be formed due to heating and subsequent decomposition or due to acidification of the corresponding acids and salts. In general all chlorooxides must be considered explosive compounds, as they all are strong oxidizers and usually very unstable. The salts of oxychloric acids behave similarly, and especially the sodium and potassium perchlorates are well-known as very powerful oxidizers. Which chemist or chemical engineer does not know the interesting explosive power of a finely divided mixture of potassium perchlorate and carbohydrates, and how many schoolboys and girls have been hurt by the unexpected explosion of the mixture, especially in confined conditions? As an example the formation of oxygen, chlorine, hypochloric acid or dichloromonoxide from a sodium hypochlorite solution is demonstrated below:



Depending on the conditions all these reactions can occur, producing gases that have a great oxidizing power.

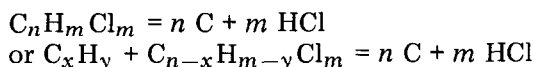
Sodium hypochlorite, that is generally produced by chlorination of a sodium hydroxide solution, presents an extra danger if the solution is heated, as disproportionation to sodium chlorate easily occurs (see the household accident stated below).

Not only chlorine itself, but chlorinated hydrocarbons also give very fast reactions with many elements and compounds, sometimes resulting in an explosion or an explosive decomposition. The best-known cases are the reaction of aluminium with chlorohydrocarbons and the reaction with strongly alkaline compounds. With aluminium metal, aluminium trichloride is formed which again is capable of catalysing quite a number of (usually exothermic) condensation reactions. This effect will be most pronounced, if for instance aromatic compounds are also present. In the reaction of chlorinated hydrocarbons with strongly alkaline compounds the highly unstable (mono- and di-) chloroacetylides are formed:



These two substances explode or detonate spontaneously upon contact with many substances, including air and oxygen. As the compound itself decomposes to carbon and chlorine or hydrochloric acid, ignition of chloroacetylides can be very dangerous, as there is no way to stop the detonation. Inerting with very large amounts of inert gas is the only preventive measure possible.

A number of other chlorohydrocarbons or mixtures thereof with hydrocarbons are capable of an exothermic decomposition reaction, especially when the ratio of hydrogen and chlorine in the mixture equals unity. The net result is the formation of carbon and hydrogenchloride, sometimes at an explosive speed, e.g.:



Methylene chloride and trichloroethylene can be mentioned as an example [26,30].

Moreover, during the combustion of a number of chlorinated hydrocarbons in oxygen or air some chlorine can be formed, apart from very small quantities of phosgene (a maximum level of 20–40 parts per million has been measured [31]).

Reaction of chlorine with some fluorine compounds may lead to an exchange of halogen, in some cases with explosive characteristics.

Cases

There have been numerous accidents in operations using chlorine, some of them related to chlorine itself and some others caused by chlorinated hydrocarbons. Statesir [30] describes a number of accidents that occurred with chlorine in a polypropylene filter upon contact with silicone oil, dibutylphthalate, hydrocarbons, glycerine, etc. A few more cases are reported below although in some of them there was no damage, and attention will be focussed on the basic problems of the handling of chlorine and chlorohydrocarbons with other components.

Chloroacetylenes

A tank containing sulphuric acid, used for drying a chlorohydrocarbon, was overfilled due to corrosion and subsequent failure of a separation wall. The material was pushed into the vent heater to a chlorine scrubber containing sodium hydroxide. It was decided to purge the header with air and during this purging procedure an explosion occurred in the scrubber. The cause was the formation of chloroacetylene, an unstable component that ignites (explodes) spontaneously upon contact with air. In the laboratory the explosion was repeated with the material recovered from the plant and the presence of chloroacetylene was proven. An analogous case was already reported in Ref. [32], describing an explosion of trichloroethylene with sodium hydroxide.

During an experiment with a mixture of methyl chloride and chlorine the gas had to be scrubbed to remove the chlorine. The gas, containing a stoichiometric amount of methyl chloride, was led through an erlenmeyer flask with a sodium hydroxide solution of 10–15%. During this operation the analyst observed that not only the chlorine but also the methyl chloride was completely absorbed. After some time the colour of the solution suddenly changed and an explosion occurred, leaving the flask intact but pushing all the liquid out. The remaining liquid was completely black owing to excessive carbon formation. In this case also chloroacetylenes are considered to have been the cause of the explosion. This experiment could be repeated very easily.

In a chemical sewer two different waste streams were mixed. During drainage of a stream containing chlorohydrocarbons, several explosions occurred and a black smoke above the sewer was observed by an operator. In this accident also chloroacetylenes must be considered the cause of the explosion since the chlorohydrocarbon-containing waste was mixed with a highly caustic waste.

Nitrogen trichloride

In the laboratory a solution containing ammonium chloride was chlorinated with sodium hypochlorite. It was known that at the reaction temperature of 80°C nitrogen trichloride was formed. As the first drops of nitrogen trichloride appeared, the experimental set-up showed a leak. The experiment was stopped and the leaking joint was cleaned. At that moment no liquid nitrogen trichloride was present, but when the clamp was placed on again, a detonation occurred and the complete set-up was destroyed. Analysis of a similar experiment proved that up to 40% of nitrogen trichloride could have been present in the gas phase as a result of the reaction at 80°C and was still present after some minutes [29].

Wrong design

In a plant a mixture of methyl chloride and chlorine was prepared in a construction schematically presented in Fig. 1. The flow was highly turbulent, so backmixing was not taken into account in the design phase. The gas temperature was 80°C and a trip was installed at a level of 150°C. Some time after start-up instabilities in the temperatures behind the bend were observed and a trip followed. Upon investigation of the instabilities the presence of a wake was considered. Chlorine was flowing back into the wake, forming an explosive mixture after some time. Due to self-heating the temperature rose and the wake expanded causing local ignition and/or reaction, registered as instabilities. The wake, being hotter than the gas itself, was partly refreshed by the intake of fresh methyl chloride and chlorine. When the autoignition temperature was reached, the mixture ignited and in turn caused ignition of the diffusive layer between chlorine and methyl chloride, giving a diffusion flame. Although the flame must

have been blown off, the trip action closed the chlorine feed and the reaction was stopped. The remedy in this case was replacing the tip of the chlorine inlet tube with a nozzle and elongation of the tube. After installation of this altered inlet tube no more trips due to high temperature were observed.

Wrong procedure

During start-up of a chlorination plant some problems arose and the start-up was terminated after the moment that both the chlorine and the organic material had been fed to the reactor, but the actual reaction had not yet started. In the procedure no clear-cut purging procedure for this situation was present, so after handling the problem the start-up was repeated. A short while after the reaction was started an explosion occurred inside the apparatus, damaging part of the internals of the next column. The ignition must have been caused by the hot gases from the reactor that came into contact with the gas mixture that was present from the previous attempt. The remedy in this case was to design a proper purging procedure for those cases where the start-up had to be interrupted before the chlorination reaction was started.

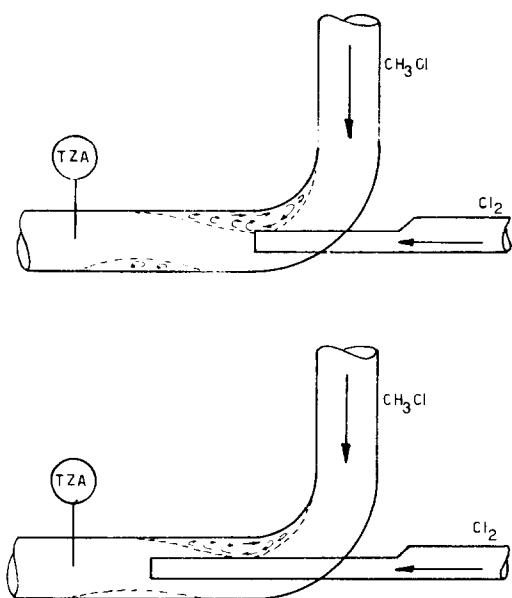


Fig. 1. Mixing point of methyl chloride and chlorine. Top: the situation causing spontaneous ignitions; bottom: the revised inlet pipe.

Suction of material in chlorine, or vice versa

Organics from a pressurized experimental set-up were sucked into a chlorine cylinder of approximately 70 l volume. After a while a vigorous

explosion occurred, completely demolishing the cylinder as well as its surroundings and laboratory equipment. In this case neither a one-way valve nor an empty containment vessel had been placed in the chlorine feed line. Due to the pressure difference caused by the chlorine absorption as a result of the reaction, the organic material entered the cylinder and exploded, possibly due to a thermal explosion.

A similar incident occurred in a chemical plant, caused by the pressure difference between two feed lines, one of which was containing organics and the other liquid chlorine. The organics were driven into the chlorine tank through a leaking valve and an explosion of the chlorine tank occurred, causing a massive chlorine emission.

The following situation once was believed to be the cause of an explosion of a chlorine container. Water was possibly sucked into a chlorine container. Chlorine will dissolve in water, forming hydrochloric acid and hypochlorous acid. These acids attack the steel and hydrogen is formed. The reaction could proceed to a very large extent as long as the iron chloride formed was dissolved in the water and/or the liquid chlorine. (The reaction of the ferric chloride with steel also highly accelerates the corrosion.) When the hydrogen pressure has reached 0.35 bar at ambient temperatures, the gas phase above the chlorine is explosive. The optimal situation for an explosion occurs when the hydrogen pressure is approximately 7 bar, giving a total pressure of approximately 14 bar. The latter mixture could give an explosion (maximum pressure approximately 140 bar) or even a detonation (shock-wave pressures of above 200 bar side-on and above 400 bar face-on pressure). These pressures are certainly above the bursting pressure of the chlorine container. Ignition could be achieved by local heating, a flash-back of flame through the valve (this mixture has a very small quenching diameter) or even due to catalytic ignition on an active site of the steel wall formed by corrosion.

Wrong combination of materials or contamination

The Manufacturing Chemists Association [33] describe the explosive reaction between chloroform and acetone in alkaline circumstances, giving a number of products, i.e., chloretone, mesityloxide and phorone. In Ref. [34] a fatal explosion is described with *N*-halogenimides in organic reactions. Apart from the direct results of the explosions, the environmental and toxic aspects of this type of reaction are also very unpleasant. The Seveso explosion is very characteristic of this type of hazard, giving at first an explosion followed by a massive emission of extremely toxic material (TCDD, tetrachloro-dibenzo-dioxin) [35].

Wrong material choice

The wrong choice of materials can present serious problems as is evident from the following case. A large chlorine release of approximately 3–7 tons occurred when a fill-in piece of PVC instead of steel was installed and

after several weeks had become brittle and fractured spontaneously. The line contained liquid chlorine at a pressure of approximately 7 bar.

Scarborough describes in Ref. [36] the explosion of an aluminium pump-house that reacted violently with the halogenated hydrocarbons that were pumped with it.

Household accident

Cooking the evening meal, consisting of a hotchpotch of kale and potatoes, a housewife in the centre of Holland found out that she had forgotten to get some goods from the grocery. So she went to fetch them (she tried to do it quickly). Returning home, she found that the contents of the pan had become rather black and smoky due to overheating caused by an obvious lack of water in the pan. While bothering about the black cake that got stuck, she suddenly remembered an old remedy her mother had told her, namely cleaning the pan by boiling a sodium hypochlorite solution (bleaching solution) in it. As it was a thick layer, she took a full litre of solution and put the pan over an electric heater in the bicycle shed (because of the smell), and went shopping again to get a meal for her family. When she returned home, the firemen had just finished their job, securing the situation after they had been alarmed by neighbours who had heard a heavy explosion.

The pan had again boiled completely dry (obviously, the store was far away). As stated before, the decomposition of sodium hypochlorite under certain conditions gives sodium chlorate which in this case was impregnated perfectly into the hotchpotch cake, consisting of carbon and carbohydrates. The electric heater provided enough energy to ignite the mixture and the explosion launched the lid through the roof, while the pan fractured the heating plate and damaged the washing machine it was placed on. (Moral lesson: Don't prepare a hotchpotch, if you have forgotten to do your shopping.)

Survey of problem fields

Mixtures of chlorine with organics are very likely to be subject to a thermal runaway or a thermal explosion, both in the gaseous and the liquid phase. Liquid chlorine is easily dissolved in many organic solvents and, conversely, chlorine is easily absorbed in many organic liquids. These mixtures, especially if the mixture is capable of forming a stoichiometric amount of carbon and hydrochloric acid and/or carbon tetrachloride and perchloroethylene, must in general be treated as condensed phase explosives. If the mixture is of stoichiometric composition, a condensed phase detonation is a very real danger and will almost certainly cause serious damage not only to the process equipment, but also to the surroundings owing to the shock-wave arising from such detonation. The same possibilities of both explosion and detonation are present in gaseous mixtures (see Tables 2 and 3). The damage caused in these cases can also be very substantial, but in general its extent will be less than with condensed systems.

When a mixture of a hydrocarbon and a chlorohydrocarbon is formed with air or oxygen and the number of chlorine and hydrogen atoms in the mixture is more or less equal, there is a serious explosion and detonation problem. A mixture of 6.85% methane in oxygen does not detonate, whereas a mixture of 6.85% methane and 6.85% carbon tetrachloride in oxygen will detonate at a velocity of 1500 m/s. In contrast with the general thought, the chlorohydrocarbon does in this case not reduce the fire and explosion hazards, but strongly enhances them, as the mixture will possibly be sensitive to a detonation [25,26].

The containment of the chlorine has to be well designed for its purpose, with respect both to the materials (to prevent reaction) and to the construction (prevention of liquid chlorine pools in gaseous phase systems). Storage and/or handling of chlorine could give trouble when water is present together with steel or other unstable metals, although absolutely dry chlorine might also present a serious corrosion problem. Corrosion of steel caused by acidic water can form hydrogen in vessels containing chlorine. The pressure will possibly rise due to the partial pressure of the hydrogen and/or as a result of an ignition and subsequent explosion of the hydrogen—chlorine mixture. Catalytic hot spots in the steel confinement can cause a chlorine—iron fire at even very moderate temperatures (190°C), causing loss of confinement and subsequent emissions. Titanium ignites spontaneously upon contact with chlorine if the chlorine is dry.

Chlorine causes serious corrosion problems, resulting in valves that cannot be closed or opened any more, and check-valves that remain open for both directions of flow because they got stuck. The formation of volatile metal chlorides may cause plugging of lines and partial plugging of orifices of flow meters, resulting in incorrect readings and, therefore, in some cases leading to incorrect (and possibly explosive) mixtures. Luckily this type of plugging occurs rather slowly, so there will be a gradual change that should be noticed by the plant personnel. In systems containing organics and chlorine, catalytic spots inside the apparatus (especially steel and carbon) might in some cases cause a local reaction producing carbon that is capable of suddenly plugging lines, valves, measuring devices, etc.

For the reasons mentioned before a number of the conventional flame traps (crimped ribbon and porous plate) cannot always be used in chlorine service. Immersion type flame traps are recommended [37], but maintaining a high gas velocity to prevent flash-back can also be a satisfactory solution. In many cases the apparatus has to be designed to withstand an accidental explosion so as to give assurance that the plant is safe.

When chlorine, or a compound capable of giving free chlorine such as sodium hypochlorite, can come into contact with nitrogen-containing compounds the formation of (liquid) nitrogen trichloride is very likely, especially under acidic conditions, even at temperatures of 80°C and above.

Chlorohydrocarbons can also cause a lot of trouble, even in the absence of free chlorine. It is commonly known that unstabilized chlorohydrocar-

bons can react with, e.g., aluminium, even explosively if it is finely divided. This risk is of particular importance when chlorohydrocarbons are recovered by distillation, while omitting the correct stabilizing procedures.

Halogenated hydrocarbons can react very violently with many organic compounds or with themselves if the amount of hydrogen and halogen atoms in the mixture is equal, or if a halogen transfer is possible (e.g. fluorine and chlorine).

Chlorohydrate, a solid compound of chlorine and water (formation of which is possible below 28.3°C), is a very dangerous substance, as the compound can form in cooling operations and cause blocking of lines, etc. Large amounts of chlorine in the form of chlorohydrate can be present after an installation has been flushed for repair. Upon temperature rise or due to a reaction, dangerous quantities of chlorine can evolve from an installation that is believed to be chlorine-free.

An often misunderstood problem occurs when chlorinated hydrocarbons are mixed with hydrocarbons or oxygenated hydrocarbons. In many cases the flammability of the mixture is not lowered by the addition of the halogenated hydrocarbon, but is enhanced [8,12,14,25,26]. The reason for this behaviour is very simply that, although many halogenated hydrocarbons have no flash point and/or are not flammable at ordinary temperatures, they still contribute to the combustible contents of the gas phase above the mixture. Nevertheless, the flammability hazards of mixtures with halogenated hydrocarbons are reduced as the ignition energies of these mixtures are usually higher than those of the non-halogenated solvents.

Conclusion

From the information given in this paper it is clear that in chlorine-containing systems a number of hazardous situations are possible, so there is a risk of damage to people, installation and the environment. However, when sufficient care is taken, especially in the design and construction stage, but also during the handling of free and bound chlorine-containing systems, explosions and fires are in general avoidable or at least containable so that the damage is minimized.

References

- 1 A.S. Mal'tseva, A.I. Rozlovskii and Yu.Ye. Frolov, Explosion hazard presented by systems containing free and bound chlorine, *Zh. Vses. Khim. O-Va*, 19(5) (1974) 542-551.
- 2 Yu.Ye. Frolov, A.S. Mal'tseva, A.N. Baratov and A.I. Rozlovskii, Certain laws governing the self-combustion of mixtures of chlorine and hydrogen, *Khim. Prom.*, 1977(7) 530-532.
- 3 J.M. Kuchta, A.L. Furno, A. Bartkowiak and G.H. Martindill, Effect of pressure and temperature on flammability limits of chlorinated hydrocarbons in oxygen-nitrogen and nitrogen tetroxide-nitrogen atmospheres, *J. Chem. Eng. Data*, 13(3) (1968) 421-428.

- 4 T. Grewer, Untersuchungen ueber die Chlor—Methan-Verbrennung, Diplomarbeit Universitaet Goettingen, 1956; T. Grewer, Zuendgrenze von Chlor—Methan-Gemischen, in: Wandel in der Chemischen Technik, Farbwerke Hoechst A.G., 1963, pp. 236—238.
- 5 A.S. Mal'tseva, Yu.Ye. Frolov and V.L. Sushchinskiy, Concentration limits of hydrocarbon—chlorine mixtures, Soviet Chem. Ind., 47(1) (1971) 23—25.
- 6 A.S. Mal'tseva, Yu.Ye. Frolov and V.M. Serdechkin, Explosive limits of mixtures of methane and its chloro-derivatives with oxygen and chlorine, Khim. Prom., 1968(8) 26—29.
- 7 K. Griesbaum and D. Hoenicke, Bestimmung der unteren Explosionsgrenze von Chlorkohlenwasserstoffen, Chem.-Ing.-Tech., 53(10) (1981) 798—799.
- 8 R.D. Coffee, P.C. Vogel, Jr. and J.J. Wheeler, Flammability characteristics of methylene chloride (dichloromethane), J. Chem. Eng. Data, 17(1) (1972) 89—93.
- 9 J.R. Grove, J.C. Patel and P. Webster, Flammability of halogenated hydrocarbons, Inst. Chem. Eng. SS, 33 (1972) 12—16.
- 10 K.S. Willson and W.O. Walker, Flammability limits in air. Methyl chloride and mixtures of methyl chloride with dichlorodifluoromethane, Ind. Eng. Chem., 36(5) (1944) 466—468.
- 11 R.L. Daniel, Chlorination hazards, Chem. Eng. Prog., Loss. Prev., 7 (1973) 74—78.
- 12 R. Callaerts, Flammability of blends of acetates and chlorinated hydrocarbons, J. Fire Flammability, 12 (1981) 272—280.
- 13 R.F. Simmons and H.G. Wolfhard, The structure of chlorine flames, ARS J., 27 (1957) 44—48.
- 14 J.R. Downey, Jr., Flammability of methylene chloride, Chem. Eng. News, (February 21, 1983) 2.
- 15 A.W. Umland, Explosive limits of hydrogen—chlorine mixtures, J. Electrochem. Soc., 101(12) (1954) 626—631.
- 16 V.N. Antonov, Yu.Ye. Frolov, A.I. Rozlovskii and A.S. Mal'tseva, Dangers of explosions in mixtures of hydrogen and chlorine, Khim. Prom., 1974(3) 205—208.
- 17 A.V. Steblev, A.S. Mal'tseva, A.I. Rozlovskii and Yu.Ye. Frolov, Combustion of chlorine—hydrogen mixtures in pipes, Khim. Prom., 1976(2) 135—138.
- 18 R.F. Schwab and W.H. Doyle, Hazards of electrolytic chlorine plants, Electrochem. Technol., 5(5/6) (1967) 228—236.
- 19 H. Hagemann, Einfluss der Gaszusammensetzung auf die Verflueissigung von Chlor bei hohem Verflueissigungsgrad, Chem.-Ing.-Tech., 39(12) (1967) 744—747.
- 20 W.C. Eichelberger, B.N. Smura and W.R. Bergenn, Explosions and detonations in chlorine production, Chem. Eng. Prog., 57(8) (1961) 94—97.
- 21 Yu.Ye. Frolov, A.S. Mal'tseva, V.M. Serdechkin, K.E. Fedotov and A.I. Rozlovskii, Some features of hydrogen-lean mixtures with chlorine, Khim. Prom., 1976(5) 358—360.
- 22 K. Munke, Explosionsverhalten des Systems Chlor—Wasserstoff und seiner Beimengungen, Chem. Technol., 26(5) (1974) 292—295.
- 23 T. Dokter, Flammability limits of the system chloromethane—dichloromethane—hydrogenchloride—chlorine, J. Hazardous Materials, 6(3) (1982) 289—297.
- 24 H. Steen and T. Redeker, Explosionsgefahren beim Umgang mit Chlorkohlenwasserstoffen und deren Gemischen mit brennbaren Fluessigkeiten, Chem.-Ing.-Tech., 47(6) (1975) 263.
- 25 H.J. Heinrich, Fortpflanzung von Detonationswellen in Gemischen von Chlorkohlenwasserstoff-Daempfen mit O₂ und N₂, Chem.-Ing.-Tech., 41(11) (1969) 655—662.
- 26 M. Hattwig, Fortpflanzung von Flammen und Detonationen in Gemischen von Chlorkohlenwasserstoffdaempfen mit O₂ und N₂, Mitteilungenblatt BAM, (1969) 293—296.
- 27 D. Pawel, Untersuchungen ueber den Anlauf von Gasdetonationen und ueber Detonationsgrenzen. Dissertation Universitaet Goettingen, 1971.

- 28 Automotive ignition system operation in a chlorine contaminated environment, Report 2219-75-122, 1975 (via Dutch Ministry of Social Affairs).
- 29 T. Dokter, Formation of NCl_3 and N_2O in the reaction of NaOCl and nitrogen compounds, to be submitted to J. Hazardous Materials.
- 30 W.A. Statesir, Explosive reactivity of organics and chlorine, *Loss Prev.*, 7 (1973) 114–120.
- 31 M.M. O'Mara, L.B. Crider and R.L. Daniel, Combustion products from vinyl chloride monomer, *Amer. Ind. Hyg. Assoc. J.*, 32(3) (1971) 153–156; D.L. Dowell, Handling vinyl chloride emergencies, *Loss Prev.*, 5 (1971) 29–31.
- 32 Anon., Safety-inspired solvent change harbors hidden fire hazard, *Chem. Proces.*, 27(14) (1964) 103.
- 33 Anon., Acetone and chloroform: an explosive mixture, *Manuf. Chem. Assoc.*, 4 (April 1975) case history 1661.
- 34 R.H. Martin, Dangers attendant on the use of *N*-halogenimides in organic reactions, *Nature*, 168 (July 7, 1951) 32.
- 35 J. Sambeth, What really happened at Seveso, *Chem. Eng.* 90(10) (1983) 45–47.
- 36 D. Scarborough, Recognizing the hazards of HHC solvents, *Prod. Finish.*, 47(1) (1982) 66–71.
- 37 G.G. Boerger, M. Schweitzer and E. Schellmann, Durchzuensicherheit von Tauchsicherungen, *Chem.-Ing.-Tech.*, 52(12) (1980) 982–983.