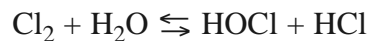


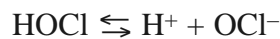
6.9.3 Chlorine

6.9.3.1 Chemistry

Chlorine, whether in the form of pure chlorine gas from a cylinder, sodium hypochlorite or calcium hypochlorite, dissolves in water to form hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻). For example, chlorine gas dissolves rapidly in water, initially forming hypochlorous and hydrochloric acids:

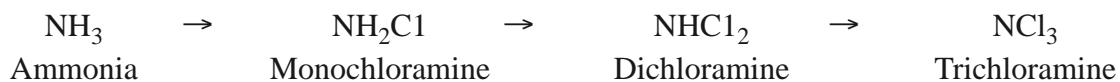


Hypochlorous acid is a weak acid which undergoes partial dissociation to produce a hydrogen ion (H⁺) and a hypochlorite ion (OCl⁻):

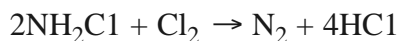


The total concentration of chlorine, hypochlorous acid and hypochlorite ions is referred to as the 'free available chlorine'. If ammonia is present in the raw water, the hypochlorous acid can react to produce chloramines. The total concentration of the chloramines and any organic nitrogen chlorine-containing compounds is referred to as the 'combined available chlorine'. Combined available chlorine is a less powerful disinfectant than free available chlorine but gives a more persistent residual.

Formation of combined chlorine is due to a sequence of reactions. Hydrogen in ammonia is progressively replaced by chlorine as follows:



If a large chlorine dose is applied (relative to ammonia), as is practised in breakpoint chlorination, then nitrogen is formed.



The effectiveness of chlorine for disinfection depends on the form of chlorine, its concentration and the contact time. Hypochlorous acid is a more powerful disinfectant than the hypochlorite ion and chlorination is usually practised at values of pH favourable to its formation. The World Health Organization recommends that for the effective disinfection of drinking water "the pH should preferably be less than 8.0 and the contact time greater than 30 minutes, resulting in a free chlorine residual of 0.2 to 0.5 mg/l".

Chlorination processes need to be carefully controlled in order to minimise problems with complaints of taste and odour. There may also be a need to control the formation of THMs (see Section 2.4.6). Therefore, for small supplies, consideration should be given to using alternatives to chlorination, such as UV.

6.9.3.2 Sources of chlorine

Chlorination can be achieved by using liquefied chlorine gas, sodium hypochlorite solution or calcium hypochlorite granules. Chlorine gas is very reactive and highly toxic and must be carefully stored and handled. It is used for treatment of large public supplies but the inherent danger of using chlorine gas has resulted in an increased use of sodium hypochlorite or the electrolysis of brine (electro-chlorination) as alternative sources of chlorine.

The use of chlorine gas for treatment of small water supplies is not recommended. Gas chlorination is generally not appropriate for supplies of less than 10 m³/d or where the available head is less than about 4 m. Leaks of chlorine gas are very dangerous. A separate area is necessary for storage of chlorine gas and an alarm system to detect leakage of chlorine must be installed. It is common practice to install alarm systems to indicate failure of the chlorine injector system or carrier water flow.

Liquefied chlorine gas is supplied in pressurised containers. The gas is withdrawn from the cylinder and is dosed into water by a chlorinator, which both controls and measures the gas flow rate.

Sodium hypochlorite solution (14 to 15% by mass (m/m) available chlorine) can be delivered to site in drums. No more than one month's supply should be delivered at one time, as its decomposition (particularly on exposure to light) results in a loss of available chlorine and an increase in concentration of chlorate, relative to chlorine.

Alternatively, sodium hypochlorite solution (0.5 to 1.0% mass per volume (m/V) available chlorine) can be generated on site by the electrolysis of brine (sodium chloride solution). A typical electrochlorination system consists of a water softener, a salt saturator, a voltage rectifier, an electrolysis cell and a storage tank containing up to three days' supply of hypochlorite solution. Hydrogen, which is produced during electrolysis, must be vented safely. These systems are compact and eliminate the need to store and handle the toxic and corrosive chlorination chemicals.

There is a wide choice of equipment available for dosing sodium hypochlorite solution. Simple gravity-fed systems in which sodium hypochlorite solution is dripped at a constant rate into a tank of water have been used successfully and have proven reliable provided that the rate of flow into supply and the chlorine demand of the water are constant. Where the flow is more variable, water-powered hypochlorinators that adjust the flow of sodium hypochlorite proportionately to the flow of water may be suitable. Electric dosing pumps can operate under flow proportional or chlorine residual control and thus maintain a consistent chlorine residual under conditions of variable flow or chlorine demand.

6.9.3.2 Sources of chlorine (continued)

Calcium hypochlorite can be supplied in powdered, granular or tablet form (65 to 70% m/m available chlorine). Calcium hypochlorite is stable when dry and several months' supply can be stored. It will however react with moisture in the air to form chlorine gas. Calcium hypochlorite dosers are relatively simple. Most allow calcium hypochlorite to dissolve in a known volume of make-up water, which is then mixed with the main supply. Tablets are most commonly used, as their rate of dissolution is predictable. Control of dosage (proportional to the rate of dissolution) is often limited to changing the depth of immersion of the tablets in the make-up water or to changing the proportion of the make-up water to total flow.

6.9.3.3 Methods of chlorination

Several regimes of chlorination can be used, including marginal (simple) chlorination, breakpoint chlorination, superchlorination/dechlorination and chloramination. On small supplies, it is probable that only marginal chlorination would be used in most cases. Marginal chlorination involves the dosing of chlorine to produce a suitable residual free available chlorine concentration.

Breakpoint chlorination could be used for removal of ammonia. Sufficient chlorine is added to exceed the demand for chloramine production and to ensure a free available chlorine residual. The chlorine dose must be carefully controlled to avoid forming dichloramine and nitrogen trichloride which can cause taste and odour problems. Breakpoint chlorination requires a dose of around 10 mg/l chlorine dosed per mg/l ammonia removed – the actual dose depends on water quality and has to be determined for each water.

The resultant free available chlorine residual should remain in the range 0.2 to 0.5 mg/l. It is recommended that the contact time should be at least 30 minutes. The design of the contact system is very important. Applied chlorine must be mixed rapidly with the water and the system must not permit short-circuiting or retention in dead zones.

6.9.3.4 Control of chlorination

Residual control is the most common method of control where chlorine is dosed continuously into the water. If the quality of the water and hence the chlorine demand varies appreciably, it is necessary to use a control system to maintain a constant chlorine residual. A sample of chlorinated water is withdrawn downstream of the chlorination system and the chlorine residual in the treated water is monitored continuously. The signal from the chlorine analyser system is used to adjust the chlorine dose thus maintaining the required residual chlorine concentration. Where water quality is invariably good, constant rate control or flow proportional control may be appropriate. In the former, a constant dose of chlorine is applied and in the latter a chlorine dose proportional to the flow of water is applied automatically under control of a signal from the flow sensor.

6.9.4 Ozone

Ozone is a powerful oxidant and disinfectant that effectively destroys bacteria and viruses. It is also more effective than chlorine in the destruction of *Cryptosporidium* oocysts. However it cannot be relied upon as the sole means of disinfection of waters that may contain *Cryptosporidium* under the conditions of dosing and water temperature normally used and found in the UK. Ozone may also reduce levels of colour, taste and odour in water. Ozonation tends to increase the concentration of Assimilable Organic Carbon (AOC), i.e. that fraction of the total organic carbon which can be utilised by bacteria. This can lead to multiplication of bacteria within the distribution system unless the AOC concentration is reduced by adsorption on granular activated carbon filters.

Ozone is a gas produced by the discharge of an alternating current through dry air. Small units can operate from a 240 Volt mains supply but larger installations require 3 phase 415 Volt supplies or higher. The ozone-containing air is mixed with the raw water in a contact column. For effective disinfection, the ozone contact system should give at least 4 minutes retention time and the ozone residual should be at least 0.4 mg/l throughout the contact period. Ozone decomposes rapidly and does not leave a persistent residual. Unless the water is used immediately, it is advisable to provide a disinfectant residual by applying a small dose of chlorine. Ozone gas is highly toxic and any excess in the vent gases from the contactor must be destroyed using a thermal or catalytic destructor.

Ozone reacts with many organic and inorganic constituents of water, thus there is an ozone demand (analogous to a chlorine demand) that must be satisfied and the ozone dose required should be determined by trials. Ozonation does not produce THMs but does form bromate if bromine compounds are present. The identity and toxicity of many of the organic oxidation products of ozone are unknown.

Small-scale package ozonation equipment is available that could be suitable for treatment of small water supplies. However, ozone is not widely used because of the high power requirements, complexity of the equipment and relatively high capital cost.