DRINKING WATER TREATMENT CHEMICALS –
FACT SHEETS

Chlorine

(endorsed 2005)

Chlorine is widely used as a primary disinfectant in the treatment of drinking water and to provide secondary disinfection in reticulation. It is also used to oxidise metals, to break down organics and to minimise biofouling. Chlorine produces potentially harmful disinfection by-products with some organics.

GENERAL DESCRIPTION

Chlorine, Cl_2, is a dense, greenish-yellow, diatomic gas with a pungent and irritating odour. It is noncombustible, but supports combustion as an oxidizing agent. The liquefaction pressure of chlorine is 7.86 atm (25°C).

Chlorine is relatively inexpensive and easy to use, although the risks associated with its transportation, storage and handling must be managed. Liquefied chlorine gas is supplied in pressurised containers of varying sizes, typically 70 kg and 990 kg. Free chlorine can also be generated on-site from electrolysis of sodium chloride solutions (brine).

Appropriate materials for handling chlorine gas include steel, copper and black iron. Aqueous chlorine can be stored in fibreglass-reinforced plastic or polyvinyl chloride.

CHEMISTRY

Chlorine is manufactured by the electrolytic dissociation of salt (sodium chloride), using mercury, diaphragm or membrane cells.

The dissolution of chlorine gas in water results in rapid hydrolysis, forming chloride ion (Cl^-), and hypochlorous acid (HOCl). Being a weak acid, HOCl is partially dissociated to hypochlorite ion (OCl^-). The degree of dissociation in equation 2 varies with temperature and pH. An increase in pH will shift the equilibrium to the right.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (1)$$

$$HOCl \Leftrightarrow H^+ + OCl^- \qquad (2)$$

The sum of the three species (i.e. Cl_2, HOCl and OCl^-) is referred to as 'free available chlorine' (FAC). The concentrations of the individual species and their sum are expressed as Cl_2, in units of mg/L.

At 25°C, hypochlorous acid is the predominant species between pH 1 and pH 7.5, and hypochlorite ion predominates at pH values greater than 7.5. Oxidation reactions and disinfecting properties of chlorine tend to be more effective at low pH values, because of the predominance of hypochlorous acid, which is a stronger oxidant.

The pH of water dosed with chlorine is affected by the amount used and the alkalinity in the water. In water with low alkalinity, the pH will drop after addition of gaseous chlorine, although it will rise if sodium hypochlorite is added.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Chlorine is employed as a strong oxidant or disinfectant, and also to provide a disinfectant residual in water distribution systems.

NOTE: Important general information is contained in PART II, Chapter 8

Chlorine can be added at various points of the treatment process:

- for oxidation of organics or metals
- for disinfection purposes
- to maintain a chlorine residual in the distribution system (pre-coagulation, intermediate or postfiltration chlorination).

Doses are usually 1–5 mg/L, although 2–3 mg/L is typical. The selection of the appropriate chlorine dose should take into account the amount of disinfection by-products formed and the required C.*t* value (concentration × contact time) and chlorine residual; the WHO recommendation is 0.5 mg/L for 30 minutes. A free chlorine residual of ≥0.2 mg/L throughout the distribution system is preferred. In some systems, rechlorination is employed within the distribution system, where chlorine is added after water has left the treatment plant, to boost chlorine residuals.

Superchlorination (10–50 mg/L) may be used to disinfect or clean tanks or pipelines, or to temporarily treat tastes and odours associated with high ammonia levels. This process is usually followed by dechlorination, to chemically remove excess chlorine. Knowledge of the breakpoint phenomenon (whereby chlorine applied in sufficient doses will oxidise ammonia and eliminate chloramines, resulting in the formation of a free chlorine residual) is also necessary when dealing with water containing ammonia.

The fact sheet on ammonia discusses the use of chorine with ammonia to produce chloramines.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. The following chemical contaminants may be present in chlorine (NRC 1982, JECFA):

arsenic
carbon tetrachloride
lead
manganese
mercury
trihalomethanes

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, chlorine should be used in such a way that any contaminant or by-product formed by the use of the chemical does not exceed guideline values in the *Australian Drinking Water Guidelines*.

The use of a disinfectant such as chlorine results in the formation of free chlorine and combined chlorine residuals and disinfection by-products, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, chloral hydrate and chloropicrine. Although many specific chlorine disinfection by-products have been identified, several of the total organic halogens have yet to be identified.

Factors affecting the distribution of disinfection by-product species include pH, temperature and the levels of total organic carbon (TOC), bromide and chlorine. THMs (e.g. chloroform, bromodichloromethane, dibromochloromethane and bromoform) are the best known chlorination by-products. Chlorinated THM, HAA and HAN species generally dominate over brominated species. However, brominated species predominate in high-bromide waters.

STATUS

Chlorine was endorsed by the NHMRC for use as a drinking water treatment chemical in 1983. The revision undertaken in 2003 did not change the status of this chemical for the treatment of drinking water.

REFERENCES

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