DRINKING WATER TREATMENT CHEMICALS

Aluminium chlorohydrate

(endorsed 2005)

Aluminium chlorohydrate is used as a primary coagulant in the treatment of drinking water. It is effective over a range of pH values and forms strong floc. It is particularly effective in some low alkalinity waters.

GENERAL DESCRIPTION

Aluminium chlorohydrate, $Al_2(OH)_5Cl$ (also known as ACH, polyaluminium chlorohydrate or aluminium chlorhydroxide), solution is a clear colourless, odourless liquid. It has a specific gravity of 1.32–1.35 at 25°C, a pH of 3.5–4.5, and is completely soluble in water.

ACH is of the polyaluminium chloride family, with a high aluminium oxide content and high basicity. It is supplied with an aluminium content of 12.2 to 12.7% (23–24% as equivalent alumina) and a basicity of 83–84%. The chemical coagulates over a wide pH range (pH 6–9) and does not usually require alkalinity adjustment.

The formula $Al_2(OH)_5Cl$ is simply a representation of the proportions of aluminium, hydroxide and chloride in the solution and it does not imply the predominant aluminium species is dimeric (see below). A generic formula for the ACH species may be given as $Al_n(OH)_mCl_{(3n-m)}$ where the m/n ration exceeds 1.05.

ACH can be stored in fibreglass-reinforced plastic, polyethylene, polypropylene or phenol formaldehyde, but can be corrosive to metals.

CHEMISTRY

ACH is manufactured from aluminium metal, which is reacted with either hydrochloric acid or aluminium chloride solution under controlled conditions.

ACH solution is a complex, dynamic mixture of positively charged polynuclear aluminium species, with no single species predominating and with molecular weights exceeding 1000. When applied to water, these species interact with and destabilises negatively charged colloidal matter, such as inorganic particles and the high molecular weight organic compounds that largely constitute natural organic matter. The polynuclear species also hydrolyse to form dense flocs of aluminium hydroxides that further act to entrap particles and remove some organic. An example of one of the many polynuclear species that may be present in ACH solution is the so called Al-13 ion that has the formula $[AlO_4.Al_{12}(OH)_{24}(H_2O)_{12}]^{13+}$.

The hydrolysis of ACH produces far less acid than the hydrolysis of aluminium sulfate owing to the very high degree of hydroxylation of the aluminium. As a result, ACH requires little of no pH correction with alkali when applied to water and results in only marginal increase in the concentration of dissolved salt.

The hydrolysis reaction proceeds as follows:

$$Al_2(OH)_5.Cl + H_2O \Leftrightarrow 2Al(OH)_3 + H^+ + Cl^-$$

As the hydrolysis reactions proceed, mononuclear hydroxide products can form polynuclear species. The reactions are complex and the species formed are quite variable. Examples of the species formed are:

- mononuclear: $Al\ OH^{2+}$, $Al(OH)_2{}^+$, $Al(OH)_3$ (solid precipitate), $Al(OH)_4{}^-$
- polynuclear: $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

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

In drinking water treatment, ACH is used as a primary coagulant. It is effective in cold temperatures and is particularly suited for use in low alkalinity raw water. It is commonly used for coagulation before membrane filtration, because this appears to reduce membrane fouling and prolong the life of the filter. The concentration of coagulant used depends on the properties of the raw water, including factors such as turbidity, dissolved organic carbon, temperature and alkalinity.

Typical ACH doses (with 23% Al_2O_3 content) are 3–100 mg/L. The actual concentration required should be determined by laboratory trials; higher doses may be required with particularly dirty water.

CONTAMINANTS

The contaminants that may be present in ACH are:

- antimony
- arsenic
- barium
- beryllium
- cadmium
- chromium
- copper
- fluoride
- iron
- lead
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- thallium
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ACH 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*.

Most of the aluminium ions resulting from the use of ACH as a coagulant are removed by conventional water treatment processes. Residual chloride is usually at low levels that do not adversely affect drinking water quality.

STATUS

ACH was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Fitzgerald JJ and Rosenberg AH (1999). Chemistry of aluminium chlorohydrate and activated aluminium chlorohydrates. In *Cosmetic Science and Technology Series, 20. Antiperspirants and deodorants*, second edition, Laden K (ed). Marcel Dekker Inc, 83–136.

Rosenberg AH, Hodges RD and Harper TL (1995). *Chemical characterisation of polyaluminium chlorides and TOC removal*. American Water Works Association Water Quality Technology Conference.

Ruehl KE (1998). Effective coagulation for variable source water: a coagulant comparison by bench and full sale evaluations. American Water Works Association Water Quality Technology Conference.

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

Aluminium sulfate (alum)

(endorsed 2005)

Aluminium sulfate (alum) is a general purpose coagulant that is used in water treatment to remove turbidity, natural organic matter (NOM) (including colour), microorganisms and many inorganic chemicals. Removal of NOM reduces the formation of disinfection by-products, because it removes the organic precursors of the by-products.

GENERAL DESCRIPTION

For use in water treatment, aluminium sulfate (alum) is generally supplied as a bulk liquid, but it can also be supplied in granular form. The concentration of the supplied liquid solution varies, and users should establish the concentration with the supplier. Typically, alum solutions contain 7.5–8.4% Al_2O_3 w/w (i.e. 43–50% w/w $Al_2(SO4)_3{\cdot}14H_2O$), and have a specific gravity of 1.28–1.34 at 20°C. Solutions at the upper end of the available strengths may become unstable at low temperatures.

Alum is also available as a crystalline solid with varying degrees of hydration (14–18 H_2O). It has a pH of 1.2–3.0 and can be stored in rubber-lined containers or in fibreglass, stainless steel (type 316) or plastic.

CHEMISTRY

Alum is produced by the reaction of sulfuric acid with an aluminium-rich ore such as refined bauxite.

In water, the aluminium ion reacts with natural alkalinity (hydroxyl or bicarbonate) or added alkalinity (lime, caustic soda or soda ash) to form aluminium hydroxide species. The hydrolysis proceeds as follows:

$$Al_2(SO_4)_3.6H_2O \Leftrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-}$$

As the hydrolysis reactions proceed, mononuclear products can form polynuclear species. The reactions are complex and the species formed are quite variable. Examples of the species formed are:

- mononuclear: $Al\ OH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ (solid precipitate), $Al(OH)_4^-$
- polynuclear: $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$

The generally positively charged Al species are available to interact with negatively charged colloidal matter in water. Such matter includes inorganic turbidity particles and the high molecular weight fraction of organic compounds present in NOM. The interaction destabilises the repulsive forces between the negatively charged particles, allowing them to collide and agglomerate to form microfloc (a process referred to as adsorption–destabilisation).

At higher concentrations of alum, metal hydroxides precipitate and can enmesh any colloidal particles in a process known as ‘sweep coagulation’, which renders water suitable for clarification. Alum has an optimum pH for coagulation of 5.5–7.5, with the lower end of the range (pH 5.5–6.2) being used for organics removal and enhanced coagulation (see below), and the higher end (pH 6.5–7.5) being used for sweep coagulation. Adsorption–destabilisation to form small floc, which can be removed by contact and direct filtration, typically occurs in the pH range 6–7.

‘Enhanced coagulation’ refers to coagulation at low pH with high doses of alum, and is used to remove NOM. The pH and alum dose need to be optimised, to maximise the removal of dissolved organic carbon (DOC).

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

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

The dose of alum used depends on the properties of the raw water, including (but not limited to) the turbidity, DOC, temperature and alkalinity. Waters of low turbidity often need higher doses of alum to bring about coagulation than more turbid waters. Indeed, waters of low turbidity and high colour are the most difficult to treat.

Typical alum doses (expressed as mg/L $Al_2(SO_4)_3 \cdot 14H_2O$) range from 5 to 200 mg/L and may even be as high as 500 mg/L if the water is particularly dirty.

The dose rate for alum is expressed in different units throughout Australia, and it is important to take this into account when comparing rates.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. In Australia, alum is produced by reacting aluminium trihydroxide or refined bauxite with sulfuric acid, and most of the impurities in the alum are derived from these raw materials.

The following chemical contaminants may be present in alum (NRC 1982):

- antimony
- arsenic
- barium
- beryllium
- cadmium
- chromium
- copper
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- thallium
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, alum 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*.

Aluminium residuals after filtration can cause floc to form in the distribution system, which can cause customer complaints. To minimise residual levels of aluminium, alum should be used at pH and dosage conditions that exceed the solubility of aluminium. At 25°C, aluminium is least soluble at a pH near 6. At colder temperatures, the pH of minimum solubility increases. For example, at 4°C, aluminium is least soluble at pH 6.5–7. Hence, if water is treated at pH 6 throughout the year, levels of residual dissolved aluminium will be higher in winter. Poor dosage selection or inadequate mixing also leads to elevated aluminium residuals.STATUS

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

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

REFERENCES

Amirtharajah A and Mills KM (1982). Rapid Mix Design for Mechanisms of Alum Coagulation. *Journal of the American Water and Wastewater Association* 74(4):210–216.

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B403-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

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Letterman RD, Amirtharajah A and O'Melia CR (1999). Coagulation and Flocculation. In: *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed), American Water Works Association, 5th edition. McGraw-Hill Professional, New York, 6.1–6.66.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

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

Ammonia

(endorsed 2005)

Ammonia, NH_3, is added to drinking water to react with chlorine to form chloramine disinfectants. Chloramination is not as powerful as chlorination but provides a longer lasting residual in the water distribution system.

GENERAL DESCRIPTION

Ammonia, NH_3, is a colourless gas or liquid, with a sharp, intensely irritating odour. It is lighter than air and easily liquefied by pressure. Ammonia has a boiling point of –33.5°C, a freezing point of –77.7°C, and a specific gravity of 0.8 as a liquid. Ammonia gas is combustible and is very soluble in water. When hydrated, ammonia can attack copper, zinc and alloys containing these metals. Ammonia can be supplied as a compressed liquid (anhydrous ammonia), dissolved in water (aqueous ammonia) or as solutions of ammonium salts (e.g. ammonium sulfate).

Gaseous ammonia is compatible with some steels, stainless steel (type 316), neoprene and monel. Aqueous ammonia can be stored in iron, steel, stainless steel, fibreglass-reinforced plastic or rubber-lined vessels.

CHEMISTRY

Ammonia is prepared commercially in vast quantities, mostly using the Haber process to combine nitrogen directly with hydrogen. It can also be made using the cyanamide process, and is produced as a by-product of the destructive distillation of coal. Most of the ammonia produced is used to make fertilisers.

The reactions between ammonia and chlorine are complex, but the simplified equations shown below are often used. The chloramines produced are monochloramine (NH_2Cl — equation 1), dichloramine ($NHCl_2$ — equation 2) and trichloramine or nitrogen trichloride (NCl_3 — equation 3).

$$NH_3^+ + HOCl \rightarrow NH_2Cl + H_2O \qquad (1)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad (2)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \qquad (3)$$

Other products are also formed, such as nitrogen (N_2) and nitrate (NO_3^-).

The sum of the concentrations of the three chloramine species is referred to as ‘combined chlorine’ and is often expressed as Cl_2, in the units of mg/L. The sum of the combined chlorine concentration and the free chlorine concentration (i.e. hypochlorous acid and hypochlorite ion) is referred to as ‘total chlorine’. The relative amounts of the three species of chloramine formed depend on the ratio of chlorine to ammonia, the pH and the temperature. Monochloramines are preferred because they do not cause the taste and odour problems that can arise with dichloramines and trichloramines. Users should refer to available data on how pH and the ratio of chlorine to ammonia affect the distribution of chloramines (see discussion in the following section), and should be aware of the breakpoint phenomenon (whereby chlorine applied in sufficient doses will oxidise ammonia and eliminate chloramines, forming a free chlorine residual).

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking-water treatment, ammonia is added with chlorine (at a fixed ratio of ammonia to chlorine) to produce chloramine disinfectants. Chloramines react with bacteria and oxidisable material more slowly than free chlorine, but last longer than free chlorine. Depending on the order and process used trihalomethanes (THMs) may form. Chloramines thus tend to be used as a secondary disinfectant to provide a disinfectant residual in the distribution system, but may also be used as a primary disinfectant if an appropriate contact time is allowed. Chloramines are particularly suited to providing disinfectant residuals in long distribution systems, where it is difficult to maintain a residual using chlorine.

To produce monochloramine, the pH should be between 8 and 9, and the chlorine to ammonia ratio should be between 3:1 and 4:1. A ratio above 4:1 may produce chlorinous odours. Ammonia may be added before or after chlorine. In primary disinfection, chlorine is usually added first, because it kills bacteria, viruses and spores much more efficiently than does monochloramine, provided that sufficient contact time is allowed for disinfection before the ammonia is added. Ammonia and chlorine can be added together, provided that contact time is sufficient to ensure disinfection.

Chloramines present in water are harmful to people on kidney dialysis and to animal species in aquaria; therefore, it is important for water utilities using chloramination to inform consumers at risk.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. Ammonia is generally supplied at 99.9 % purity or better, but the product may include a very small amount of oil (hydrocarbons), heavy metals and water.

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ammonia 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*. Free ammonia liberated in the distribution system may contribute to nitrification problems or biological growth.

Chloramines may form some halogenated organic by-products. THMs may also be produced, but to a much lesser extent than with chlorination. More information on chloramines can be obtained from the Chloramine Fact Sheet in the *Australian Drinking Water Guidelines*.

STATUS

Aqueous ammonia 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

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. American Public Health Association, Washington, DC.

Connell GF (1996). *The Chlorination/Chloramination Handbook*. Water Disinfection Series, American Water Works Association. Denver, Colorado.

Hass CN (1999). Disinfection. In *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed). American Water Works Association, 5th edition. McGraw-Hill Professional, New York, 14.1–14.60.

Lewis RJ (1993). *Hawley's Condensed Chemical Dictionary*, 12th edition. Van Nostrand Reinhold, New York.

White GC (1992). *Handbook of chlorination and alternative disinfectants*, 3rd edition. Van Nostrand Reinhold, New York.

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

Ammonium sulfate

(endorsed 2005)

Ammonium sulfate is used as a source of ammonia to react with chlorine in drinking water treatment, to form chloramines. Chloramination is not as powerful as chlorination but provides a longer lasting residual in the water distribution system.

GENERAL DESCRIPTION

Ammonium sulfate, $(NH_4)2SO_4$, is an off-white crystal which is soluble in water (up to a concentration of 10 g/L). It has a specific gravity of 1.77 (at 20°C), and is available in several grades as 60–100% effective product.

Ammonium sulfate can be stored in rubber-lined vessels or in containers made from stainless steel (type 316), neoprene, monel, fibreglass-reinforced plastic, polyethylene or polyvinyl chloride. If the ammonium sulfate is dry, cast iron can also be used.

CHEMISTRY

Ammonium sulfate is by-product of the manufacture of caprolactam (a nylon-base material), coal gas and coke. It can also be prepared by the reaction of ammonia with sulfuric acid. It dissolves in water to form ammonium hydroxide (NH_4OH — equation 1), which then releases ammonia gas (NH_3 — equation 2):

$$(NH_4)_2 + 2H_2O \rightarrow 2NH_4OH + H_2SO_4 \qquad (1)$$

$$NH_4OH \Leftrightarrow NH_3 + H_2O \qquad (2)$$

Solutions of ammonium salts or aqueous ammonia (ammonia dissolved in water) have an alkaline pH. The actual pH depends on the concentration and the temperature. It is important to vent facilities storing ammonium salt solutions, because of the formation of ammonia gas. Ammonium salt solutions and aqueous ammonia have the same characteristics; therefore, the same care should be taken during handling.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Ammonium sulfate is used as a source of ammonia for disinfection (see ammonia fact sheet for further details).

The amount of ammonium sulfate to be added can be determined by multiplying the required ammonia level by the molecular ratio of 7.77 (i.e. $(NH_4)2SO_4 = 7.77 \times NH_3$). The ammonia fact sheet includes information on levels needed for chloramination.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. Ammonium sulfate may contain moisture and insoluble material as well as the following chemical contaminants (JECFA, NRC 1982):

- aluminium
- arsenic
- chloride
- lead
- pyridine
- selenium
- iron
- nickel

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

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ammonium sulfate 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.*

Excessive dosage can lead to biological growth in distribution system (see ammonia fact sheet for further details).

STATUS

Ammonium sulfate was originally 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B302-00. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

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JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

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NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC.

White GC (1992). *Handbook of chlorination and alternative disinfectants*, 3rd edition. Van Nostrand Reinhold, New York.

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

Calcium hydroxide

(endorsed 2005)

Calcium hydroxide (hydrated lime) is used to raise pH and adjust alkalinity for coagulation optimisation, corrosion control and water softening. It can also be used to dewater sludge.

GENERAL DESCRIPTION

Calcium hydroxide, $Ca(OH)_2$ (also known as lime or hydrated lime), adds hydroxide ions to water, thereby increasing its pH and alkalinity. It is a soft, white, crystalline powder.

The hydrated lime available commercially is a powder that contains mainly calcium hydroxide, or a mixture of calcium hydroxide and magnesium hydroxide. Pure hydrated lime has a specific gravity of 2.3–2.4. The bulk density of commercial lime varies from 450 to 560 kg/m^3, and it usually contains 80–96% calcium hydroxide. Its solubility at 20°C is 0.165% (or 0.165 g/100 g of saturated solution). Hydrated lime can be stored in rubber-lined containers or in fibreglass-reinforced plastic, polyethylene, polyvinyl chloride, cast iron or steel.

CHEMISTRY

Calcium hydroxide is obtained by hydrating quicklime with sufficient water to satisfy its chemical affinity for water. Quicklime is the product of the calcination of limestone, and consists mainly of the oxides of calcium (CaO) and magnesium (MgO). Calcium hydroxide is added to water to provide hydroxide ions to raise pH and alkalinity, and to neutralise free carbon dioxide or carbonic acid. It reacts with carbon dioxide to form calcium bicarbonate.

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$$

To remove carbonate hardness, hydroxide ions are used to raise the pH of water. This causes precipitation, as bicarbonate ions are converted to the carbonate (pH > 10), precipitating calcium carbonate.

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3(s) + 2H_2O$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In production of drinking water, calcium hydroxide is used:

- at the start of the water treatment process, to adjust pH and boost alkalinity, to assist coagulation
- at the end of the treatment process, to adjust final pH and alkalinity, and to minimise corrosion
- to soften hard waters by raising the pH, and thus precipitating calcium carbonate
- with carbon dioxide, to increase soft water's resistance to pH changes during distribution and to decrease its corrosivity
- to reduce the moisture content of sludge — if the concentration of calcium hydroxide is sufficiently high it will collapse the sludge structure, helping to reduce the water content of the sludge.

Lime is usually made up as a solution or as a slurry of up to 10% concentration; a slurry with a concentration of 1–5% is most commonly employed.

Typical lime concentrations used in drinking water treatment depend on the quality of the water to be treated and the purpose of the treatment (water softening, pH adjustment, alkalinity increase). Lime concentrations can vary from 5 to 500 mg/L, and the appropriate concentration should be determined by laboratory trials.

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

Poor mixing, poor pipe design, lime scaling and impurities often lead to blockages in lime dosing systems. To overcome such problems, the design of the system should minimise areas of solids accumulation, and the dosing system should be flushed each time it is turned off with water, chlorinated water or weak acid. Regular cleaning of the batch and dosing tanks using a solution of weak acid is also recommended.

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 calcium hydroxide, depending on the source of the raw materials (JECFA, KIWA 1994, NRC 1982):

- aluminium
- arsenic
- barium
- cadmium
- chromium
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- selenium
- silica
- silver

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, calcium hydroxide 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*.

Adding lime to water can significantly raise the turbidity. It can also increase the concentrations of iron, aluminium and manganese. Thus, it is often best to add lime at the start of the water treatment process, so that any impurities added with the lime can be removed during the treatment process.

The sludge resulting from water softening consists mainly of calcium carbonate, or a mixture of calcium carbonate and magnesium hydroxide. This sludge is generally dense, stable and inert; dries well; has a solids content of about 5% from the clarifier (although it can range from 2 to 30%); and has a pH greater than 10.5.

STATUS

Calcium hydroxide 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B202-02. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

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

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

Calcium hypochlorite

(endorsed 2005)

Calcium hypochlorite is a drinking water disinfectant used only for small systems.

GENERAL DESCRIPTION

Calcium hypochlorite, $Ca(OCl)_2$, is a white crystalline solid. It has a specific gravity of 2.35, decomposes in water and alcohol, is not hygroscopic and is practically clear in a water solution. The chemical is a highly active oxidiser and is relatively stable. The oxidising capability of 1 g calcium hypochlorite (65% strength) is equivalent to the oxidising capability of 0.65 g chlorine gas.

Calcium hypochlorite is available commercially as a dry solid, with a strength of up to 74% available chlorine. In this form, it loses about 0.013% of its strength per day under normal storage conditions, although the rate can be higher if the chemical is in contact with water or is exposed to the atmosphere. It is also available in a tablet form for use in automatic feed equipment at low-flow treatment plants or for dosing of in-system reservoirs.

Appropriate handling materials for calcium hypochlorite include glass, ceramics, fibreglass-reinforced plastic, polyethylene, polyvinyl chloride. Rubber-lined containers can also be used.

CHEMISTRY

Calcium hypochlorite is formed by the addition of chlorine to a slurry of 'milk of lime' (calcium hydroxide).

Calcium hypochlorite granules dissolve in water to form hypochlorous acid (HOCl), which partially dissociates to the hypochlorite ion (OCl^-).

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2$$

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^-$$

$$OCl^- + H2O \Leftrightarrow HOCl + OH^-$$

As with the addition of chlorine gas, the relative distribution of hypochlorous acid and hypochlorite ion resulting from the addition of calcium hypochlorite to water will depend on pH and temperature.

Calcium hypochlorite is a base and therefore raises the pH of water, whereas chlorine gas produces an acidic reaction that lowers the pH of the solution. The extent of the pH change depends on the alkalinity of the water.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Calcium hypochlorite is generally used as a disinfectant in smaller water treatment plants or in new water mains or in-system reservoirs.

As a disinfectant in water systems, calcium hypochlorite must be dissolved in water before it is added to the main supply. Doses usually range from 1 to 5 mg/L (as available chlorine), with 2–3 mg/L typical. Selection of the appropriate chlorine dose should take into account the C.*t* (disinfectant concentration × contact time) and chlorine residual required, and the levels of disinfection by-products likely to be formed. A free chlorine residual of ≥0.2 mg/L throughout the distribution system is preferred. Superchlorination (doses of 10 to 50 mg/L) may be used to disinfect or clean tanks and pipelines.

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

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. Chemical contaminants that may be present in calcium hypochlorite include:

- aluminium
- arsenic
- barium
- cadmium
- chromium
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- selenium
- silica
- silver

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, calcium hypochlorite 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 calcium hypochlorite as a disinfectant results in the formation of free chlorine, combined chlorine residuals and disinfection by-products. The by-products formed include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, chloral hydrate and chloropicrin. Although many specific chlorine disinfection by-products have been identified, many of the total organic halogens are as yet unidentified.

Among the many factors affecting the species formed as disinfection by-products are pH, temperature and levels of total organic carbon (TOC), bromide and chlorine. THMs (e.g. chloroform, bromodichloromethane, dibromochloromethane and bromoform) are the most widely known chlorination by-products. Chlorinated THM, HAA and HAN species are generally found at higher levels than brominated species; however, brominated species predominate in waters containing high levels of bromides.

The disinfection by-products most likely to occur and to be of concern to health are total THMs and THM species, total HAAs and HAA species.

STATUS

Calcium hypochlorite 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B300-99. AWWA CD-ROM (April 2003). Details at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. American Public Health Association, Washington, DC.

Connell GF (1996). *The Chlorination/ Chloramination Handbook*. Water Disinfection Series, American Water Works Association, Denver.

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Calcium oxide

(endorsed 2005)

Calcium oxide is used (after hydrating to produce 'slaked lime') to correct pH and adjust alkalinity, for coagulation optimisation, corrosion control and water softening. It can also be used to assist in the dewatering of sludge.

GENERAL DESCRIPTION

Calcium oxide, CaO, is also known as calx, quicklime, unslaked lime and burnt lime. It is a grey-white, hard, odourless solid, which sometimes has a yellowish or brownish tint due to the presence of iron. It crumbles on exposure to moist air and is soluble in acid. Calcium oxide reacts with water to form calcium hydroxide (slaked lime), releasing heat as it does so.

Calcium oxide is available in several grades, and is the least expensive way of obtaining calcium hydroxide. Quicklime has a specific gravity of 3.2–3.4. Its bulk density is 1030 kg/m^3 for pebble quicklime or 1050 kg/m^3 for powder quicklime; it usually contains approximately 94% calcium oxide.

Appropriate handling materials for calcium oxide include fibreglass-reinforced plastic, polyethylene, polyvinyl chloride, cast iron and steel. Rubber-lined containers can also be used.

CHEMISTRY

Calcium oxide is formed by calcination of limestone, and it can also contain magnesium oxide, MgO. Before being used in drinking water treatment, calcium oxide must be hydrated or 'slaked' to calcium hydroxide or slaked lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Slaked lime is added to water to provide hydroxide ions to raise pH and alkalinity, and to neutralise free carbon dioxide or carbonic acid. It reacts with carbon dioxide to form calcium bicarbonate:

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$$

To remove carbonate hardness, hydroxide ions are used to raise the pH of water. This causes precipitation, as bicarbonate ions are converted to the carbonate (at $pH > 10$), precipitating calcium carbonate.

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\ (s) + 2H_2O$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In production of drinking water, slaked lime is used:

- at the start of the water treatment process, to adjust pH and boost alkalinity in order to assist coagulation
- at the end of the treatment process, to adjust final pH and alkalinity, and to minimise corrosion
- to soften hard waters by raising the pH, thus precipitating calcium carbonate;
- with carbon dioxide, to increase soft water's resistance to pH changes during distribution and to decrease its corrosivity
- to reduce the moisture content of sludge — if the concentration of calcium hydroxide is sufficiently high it will collapse the sludge structure, helping to reduce the water content of the sludge.

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

Slaked lime is usually made up as a solution or a slurry of up to 10% concentration; a slurry with a concentration of 1–5% is most commonly employed.

Typical slaked lime concentrations used in drinking water treatment depend on the quality of the water to be treated and the purpose of the treatment (e.g. water softening, pH adjustment or alkalinity increase). Slaked lime concentrations can vary from 5 to 500 mg/L, and the appropriate concentration should be determined by laboratory trials.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the source of the raw materials and on the manufacturing process. The following chemical contaminants may be present in calcium oxide (JECFA, KIWA 1994, NRC 1982):

- aluminium
- arsenic
- barium
- cadmium
- chromium
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- selenium
- silica
- silver

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, calcium oxide 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*.

Adding slaked lime to water can significantly raise the turbidity and the concentrations of iron, aluminium and manganese. Thus, it is often best to add slaked lime at the start of the water treatment process, if possible, so that any impurities added with it can be removed during the treatment process.

STATUS

Calcium oxide 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B202-02. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

KIWA (1994) *Guideline quality of materials and chemicals for drinking water supplies*. Inspectorate of Public Health and Environmental Planning, Publication 94-01. Rijswijk, The Netherlands.

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

National Lime Association (1992). *Chemical Lime Facts*, 6th edition. National Lime Association, Washington, DC.

National Lime Association (1995). *Lime: Handling, Application and Storage*, 7th edition. National Lime Association, Arlington, Virginia.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC.

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

Carbon, granulated activated

(endorsed 2005)

Granular activated carbon is used in drinking water treatment to adsorb or biologically degrade dissolved organic matter, pesticides, algal toxins and compounds causing taste or odour problems. Use of activated carbon used before disinfection reduces the formation of disinfection by-products, by reducing the amount and reactivity of organic precursors of these by-products.

GENERAL DESCRIPTION

Granular activated carbon (GAC) is a black, solid, extremely porous material that can adsorb impurities and contaminants from air and water. It has a complex, porous internal structure, with internal surface areas averaging about 900 m^2/g and a bulk density of 250–600 kg/m^3. Activated carbon is insoluble in water and organic solvents.

The properties of activated carbon depend on its degree of activation and the raw material from which it is produced. Coal, wood and coconut-based activated carbons each have different pore structures and different characteristics.

GAC may act as a biological carrier by housing bacteria in its internal honeycomb structure. When GAC filters are used in an enhanced biological mode, they are referred to as biological activated carbon (BAC) filters. BAC filters work through two mechanisms: biodegradation of contaminants (e.g. taste and odour compounds, and organics) and biological regeneration of the carbon's adsorption sites.

Dry activated carbon can be stored in cast iron or steel silos. Wet activated carbon can be stored in plastic, rubber or silicon-lined containers, or in stainless steel (type 316), monel or bronze.

CHEMISTRY

Carbon is 'activated' by heating carbonaceous material such as wood, coal or coconut husks to high temperatures in a controlled atmosphere of steam, or at moderate temperatures in the presence of chemicals such as acid.

The adsorptive properties of GAC vary with pore size, pore-size distribution, internal surface area of the pores and surface properties. The properties of the GAC available in the market are variable. In selecting an activated carbon product, it is important to consider factors such as the adsorptive capacity of the activated carbon, the desired application, abrasion resistance during backwashing and cost. The quality of the activated carbon can be determined by its ability to remove contaminants such as 2-methylisoborneol (MIB), geosmin, toxins and pesticides, and by a number of other factors that are listed below, together with typical ranges (actual values will depend on the raw material and the activation processes):

- iodine number: 900–1300 mg/g carbon
- apparent density: 0.2-0.6 g/cc
- moisture content: 3-8%
- abrasion resistance: 75-99%
- particle size distribution: 5% maximum on upper sieve
  90% minimum between sieves
  5% maximum through lower sieve
- ash content: 3–15%

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

The adsorptive capacity of activated carbon can be inferred from the iodine number, methylene blue number or molasses number.

Effective sizes of GAC are typically 0.7–1.2 mm, with a uniformity coefficient (UC) generally specified to be less than 1.8. The GAC is installed over supporting layers of sand and gravel.

After installation in the filter bed, the GAC is carefully wetted over several hours. In some carbons, significant flotation of the carbon may occur in the wetting phase, and the floating portion of GAC is removed and disposed of. The floatable component of the GAC may vary between 0 and 30%.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In water treatment, activated carbon is used to control taste and odour-causing compounds, and to remove contaminants such as nitrates, pesticides, algal toxins, disinfection by-products, organic carbon and other trace organic chemicals.

GAC is generally used as a filter medium in beds or tanks, with the water being treated as it passes through the filter. Contaminants are removed through adsorption and biological degradation. Many taste and odour compounds (e.g. 2-methylisoborneol (MIB), geosmin and 20–50% of natural organics) can be biologically degraded, and GAC filters used in this way can operate for 10–15 years. If the contaminant is not biodegradable, the GAC medium can be used continuously until its adsorption capacity is exhausted; and can then be reactivated using a thermal process (currently not available in the Australian drinking water industry). In adsorption mode, a GAC bed is effective for about 1 month to 2 years, depending on the concentration of contaminants in the water.

GAC beds can be used either before or after conventional treatment (i.e. pre-filtration or post-filtration). GAC can also be used for a combination of filtration and adsorption, either as a full GAC bed, or as a layer of sand topped with a layer of GAC medium. The process can be preceded by ozonation, which encourages biological activity on the filter (creating a BAC filter), thus prolonging the life of the filter. Ozonation generally produces water that is more biologically stable and has a lower chlorine demand.

GAC and BAC filters are designed for a specific empty bed contact time (EBCT), which typically ranges from 5 to 25 minutes. The most economic EBCT can be determined by analysing particular contaminants of concern, at either laboratory or pilot scale.

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 the ash that may be found in activated carbon:

- aluminium
- arsenic
- chromium
- iron
- lead
- manganese
- mercury
- phosphorus
- silver
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, activated carbon 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*.

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

Degraded GAC can pass through a water treatment plant, causing black specks and deposits in the distribution system, although it is unlikely that significant quantities of carbon residues will be present in finished water.

STATUS

Activated carbon 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard B604-96. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Gosselin RE, Smith, RP and Hodge HC (1984). *Clinical Toxicology of Commercial Products*, 5th edition. Williams and Wilkins, Baltimore, II-94.

IARC (International Agency for Research on Cancer) (1984). *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*. World Health Organization, Geneva, Switzerland.

NIOSH (National Institute for Occupational Safety and Health) (1984). Method 5000, Carbon Black (issued 2-15-84). In: *NIOSH Manual of Analytical Methods. Methods A-Z & Supplements*, 4th edition.

U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. U.S. Government Printing Office ,Washington, DC.

Snoeyink VL and Summers RS (1999). Adsorption of Organic Compounds. In: *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed). American Water Works Association, 5th edition. McGraw-Hill Professional, New York, 13.1–13.76.

Urfer D, Huck PM, Booth SDJ, and Coffey BM (1997) Biological Filtration for BOM and particle removal: a critical review. *AWWA Journal* 89(12) 83-98.

Carbon, powdered activated

(endorsed 2005)

Powdered activated carbon is used in drinking water treatment to adsorb dissolved organic matter, pesticides, algal toxins and compounds causing taste or odour problems. Adding activated carbon before disinfection reduces the formation of disinfection by-products, by reducing the amount and reactivity of organic precursors of these by-products.

GENERAL DESCRIPTION

Powdered activated carbon (PAC) is a black, solid, extremely porous material that can adsorb impurities and contaminants from air and water. It has a complex, porous internal structure, with internal surface areas averaging about 900 m^2/g and a bulk density of 250–600 kg/m^3. Activated carbon is insoluble in water and organic solvents.

The properties of activated carbon depend on its degree of activation and the raw material from which it is produced. Coal, wood and coconut-based activated carbons each have different pore structures and different characteristics.

Dry activated carbon can be stored in cast iron or steel silos. Wet activated carbon can be stored in plastic, rubber, or silicon-lined containers, or in stainless steel (type 316), monel or bronze.

CHEMISTRY

Carbon is 'activated' by heating carbonaceous material such as wood, coal or coconut husks to high temperatures in a controlled atmosphere of steam, or at moderate temperatures in the presence of chemicals such as acid.

The adsorptive properties of PAC vary with particle size, pore size, pore-size distribution, internal surface area of the pores and surface properties. The properties of the PAC available in the market are variable. In selecting an activated carbon product, it is important to take into account factors such as the adsorptive capacity of the activated carbon, the desired application and the cost. The quality of the activated carbon can be determined by its ability to remove contaminants such as 2-methylisoborneol (MIB), geosmin, toxins and pesticides, and by a number of other factors that are listed below, together with typical ranges (actual values will depend on the raw material and the activation processes):

- iodine number: 800–1400 mg/g carbon
- apparent density: 0.2-0.6 g/cc
- moisture content: 3-8%
- particle size distribution: 90% minimum through 100 µm mesh
  95% minimum through 200 µm mesh
- ash content: 3–15%

The adsorptive capacity of activated carbon can be inferred from the iodine number, methylene blue number or molasses number.

Effective sizes of PAC are typically 20–50 µm.

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

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, PAC can be added as a powder by dry-feed equipment; for higher dosing, it can be added as a slurry by metering pumps or feeders. It is important to add PAC early in the treatment process, before addition of chemicals such as chlorine, to ensure sufficient contact time and to avoid chemicals being adsorbed onto the carbon. For intermittent or low dosing, Ideally, PAC is added 30 minutes before coagulation; often near the raw water source. Care should be taken to avoid areas where PAC may build up (e.g. low-velocity pipes). The carbon is mixed for a short time before being removed by settling or filtration.

If PAC is added in the coagulation zone, additional PAC may be required, because the carbon can become bound in flocs, diminishing its effectiveness. Jar testing reflecting the operating conditions can determine the effective dose rate and contact time for optimal performance of PAC.

Occasionally, PAC is dosed immediately before filtration, where it reacts with organics above and within the filter bed. Care should be taken to avoid breakthrough of PAC caused by normal sludge removal processes (e.g. clarifier sludge blowdowns, flotation or filter backwashing).

The amount of PAC required will depend on the type and concentration of organics in the water. Typical values range from 2 to 60 mg/L, but can be as high as 100 mg/L. A contact time of 10–30 minutes between the PAC and the water generally removes most taste and odour compounds, but a longer time may be needed for removal of MIB and geosmin (the compounds most often linked with tastes and odours — see the fact sheet on taste and odour).

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 the ash that may be found in activated carbon:

- aluminium
- arsenic
- chromium
- copper
- iron
- lead
- manganese
- mercury
- phosphorus
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, PAC 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*.

Powdered carbon slurry applied to raw water is easily removed by other water treatment processes (e.g. by settled sludge, floated sludge or filtration). PAC can pass through a water treatment plant, causing black specks and deposits in the distribution system, although it is unlikely that significant quantities of carbon residues will be present in finished water.

STATUS

Activated carbon 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.

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

REFERENCES

AWWA (American Water Works Association)/ANSI (American National Standards Institute) (1997). Standard B604-96. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Gosselin RE, Smith, RP and Hodge HC (1984). *Clinical Toxicology of Commercial Products*, 5th edition. Williams and Wilkins, Baltimore, II-94.

IARC (International Agency for Research on Cancer) (1984). *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*. World Health Organization, Geneva, Switzerland.

NIOSH (National Institute for Occupational Safety and Health) (1984). Method 5000, Carbon Black (issued 2-15-84). In: *NIOSH Manual of Analytical Methods. Methods A-Z & Supplements*, 4th edition. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. U.S. Government Printing Office ,Washington, DC.

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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	manganese
carbon tetrachloride	mercury
lead	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.

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

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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B301-99. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. American Public Health Association, Washington, DC.

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Copper sulfate

(endorsed 2005)

Copper sulfate is an active constituent in registered algicide products used in drinking water reservoirs. There are different State and Territory environment protection regulations on the use of copper sulfate in reservoirs. Further information should be sought form the relevant State or Territory agency.

GENERAL DESCRIPTION

Copper sulfate, $CuSO_4$, is a blue crystal, or blue crystalline granule or powder, but is white when dehydrated. The chemical has a nauseous metallic taste and is poisonous. The anhydrous form contains nearly 50% copper; the commonly used pentahydrate form ($CuSO_4 \cdot 5H_2O$) contains 25.5% copper.

Appropriate handling materials for copper sulfate include fibreglass-reinforced plastic, polyethylene, polyvinyl chloride, cast iron and stainless steel. Rubber-lined and silicon-lined containers can also be used.

CHEMISTRY

Copper sulfate is the product of the reaction of sulfuric acid with copper metal, cupric oxide or basic copper salts.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Copper sulfate is an algicide, and is used to treat toxic or odorous algal blooms in water reservoirs and other water supply storages. Copper sulfate may kill aquatic plants, insects, invertebrates and fish. Copper sulfate is subject to registration and labelling requirements of the Australian Pesticides and Veterinary Medicines Authority. Copper sulfate is not registered for general use as an algicide in all jurisdictions therefore, before copper sulfate is used in a water storage system, the State or Territory environment protection authority must be advised. In some States and Territories, a licence must be obtained for its use. The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (2002) contain information on the effect of copper sulfate on various ecosystems. There is a range of alternative water treatment and storage management methods for controlling the risks of toxic algal bloom including reducing the amounts of nutrient inflow to water reservoirs.

The application of copper sulfate products to storages should be in accordance with the registered chemical label. Copper sulfate can be applied by:

- dissolving crystals of the chemical into the water using porous bags pulled by a boat
- applying the crystals directly using a hopper feeder
- spraying dissolved copper sulfate on the water surface.

To determine the appropriate dose rate and ensure efficient application, knowledge of algal habitat and distribution is needed. Experience with the use of copper sulfate to treat cyanobacteria indicates that it is best to start applying the chemical early in the morning, and to apply it during calm conditions. This is because cyanobacteria tend to be most buoyant at this time, and are likely to be near the surface.

For a stratified reservoir, calculation of the total amount of algicide to be added is based on the amount needed to treat the surface of the water body, because this is where most cyanobacteria will be located. Treatment of algae should be concentrated in areas of algae scum.

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

The amount of copper sulfate required will depend on various factors, such as pH, alkalinity and water temperature (algae are more likely to bloom in warm water).

Copper sulfate is most effective at pH values of around 8, and alkalinity less than 50 mg/L. In conditions of high alkalinity or pH, addition of an acid (e.g. citric acid) may also be needed for the copper sulfate to be effective. The concentrations of copper sulfate added are typically in the range 0.2–1 mg Cu/L, depending on the specific type of organism being controlled.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. Chemical contaminants that may be present in copper sulfate include (JECFA):

- arsenic
- chloride
- iron
- lead
- nickel

RESIDUE AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, copper sulfate 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*. A limit of 2 mg/L based on health considerations and of 1 mg/L for aesthetic considerations has been established for copper residues resulting from the use of copper sulfate.

Copper sulfate breaks down algae, resulting in the release of algal toxins and odorous substances that decay over time. Hence, a withholding period is needed after copper sulfate has been used as an algicide, and it may be necessary to monitor copper residues, toxins and odours during a follow-up period.

Copper sulfate products should not be used to treat more than half of a lake or pond at one time, in order to avoid depletion of oxygen caused by decaying vegetation. One to two weeks should be allowed between copper sulfate treatments to allow water oxygen levels to recover.

Copper entering a water treatment plant may be removed to some degree through coagulation with clarification/filtration. Elevated pH assists in copper removal.

STATUS

Copper sulfate 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B602-02. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

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

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

Ferric chloride

(endorsed 2005)

Ferric chloride is used as a primary coagulant in the treatment of drinking water, particularly when a broad coagulation pH range is required It is used to remove turbidity, natural organic matter (NOM) (including colour), microorganisms and many inorganic chemicals. Removal of NOM reduces the formation of disinfection by-products, because it removes the organic precursors of the by-products.

GENERAL DESCRIPTION

Ferric chloride, $FeCl_3$ (anhydrous) or $FeCl_3{\cdot}6H_2O$ (crystalline), has a brownish-yellow or orange colouration when in crystalline form and is very hygroscopic. In solution, it has the appearance of a dark-brown syrup. Solutions of ferric chloride are acidic and corrosive to most metals. The typical pH range of a 1% solution of ferric chloride is 3–4. The chemical is significantly more soluble in hot water (535.7 g/100 mL at 100°C) than in cold water (74.4 g/100 mL at 0°C), and is very soluble in alcohol, ether and methanol.

Ferric chloride is available as a powder and in solution at 30–42%. A 42% solution of ferric chloride has a specific gravity of 1.45 at 20°C, contains 14.5% iron and has a pH of 1–2.

Ferric chloride is highly corrosive to most metals, including stainless steel; however, it can be stored or transported in fibreglass, rubber-lined carbon steel, polyvinyl chloride, polyethylene or polypropylene.

Polytetrafluoroethylene and polyvinylidene difluoride are also suitable as lining materials.

CHEMISTRY

Ferric chloride is obtained from ores containing iron and titanium oxides. It is also produced through the reaction of chlorine gas with iron, ferrous sulfate or ferrous chloride.

The positively charged Fe species are available to interact with negatively charged colloidal matter in water. Such matter includes inorganic turbidity particles and the high molecular weight fraction of organic compounds present in natural organic matter (NOM). Fe cations interact with the natural alkalinity to form hydroxides that then act in a charge neutralisation fashion similar to that for aluminium. Charge neutralisation destabilises the repulsive forces between the negatively charged particles, allowing them to approach closely, collide and agglomerate. Metal hydroxides precipitate and can enmesh any colloidal particles. Iron floc is generally large and settles rapidly though it may be weaker than alum floc. As for aluminium, sweep coagulation can also occur at higher doses.

The stoichiometry of the precipitation of iron hydroxide is described as follows:

$$FeCl_3\ (s) \rightarrow Fe^{+3} + 3Cl^-$$

$$Fe^{+3} + 3OH^- \rightarrow Fe\ (OH)_3(s)$$

Ferric chloride is an effective coagulant at a pH between 4 and 11. When added to water, ferric chloride consumes more alkalinity than does alum.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Ferric chloride is used as a primary coagulant, especially when a broader coagulation pH range is required.

The amount of ferric chloride added depends on the properties of the raw water, including factors such as turbidity, NOM, temperature and alkalinity.

Typical ferric chloride doses are 2–100 mg/L $FeCl_3{\cdot}6H_2O$, although higher doses may be required if water

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

is particularly dirty. At high doses, product water should be tested to ensure that maximum contaminant levels have not been exceeded.

The dose rate for ferric chloride may refer to crystalline or anhydrous ferric chloride, supplied as liquid or as iron. Care should be taken when interpreting dose rates to ensure that comparisons are relevant.

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 this product (KIWA 1994, NRC 1982:

- antimony
- arsenic
- cadmium
- chromium
- cobalt
- copper
- cyanide
- lead
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- titanium
- vanadium
- zinc

Manganese concentrations in ferric chloride may be high enough to affect the treated water.

RESIDUE AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ferric chloride 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*.

Conventional water treatment processes, if optimised, remove almost all of the ferric ions produced when ferric chloride is used for coagulation. Residual chloride is usually at low levels, which do not adversely affect drinking water quality.

The presence of any ferrous iron in the product reduces its effectiveness in water treatment and increases the possibility of soluble iron carry over. This could cause post precipitation of ferric hydroxide (red water) in the distribution system.

STATUS

Ferric chloride 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B407-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater,* 20th edition. American Public Health Association, Washington, DC.

KIWA (1994) *Guideline quality of materials and chemicals for drinking water supplies*. Inspectorate of Public Health and Environmental Planning, Publication 94-01. Rijswijk, The Netherlands.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

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

Ferric sulfate

(endorsed 2005)

Ferric sulfate is used as a primary coagulant in the treatment of drinking water, particularly when a broad coagulation pH range is required. It is used to remove turbidity, natural organic matter (NOM) (including colour), microorganisms and many inorganic chemicals. Removal of NOM reduces the formation of disinfection by-products, because it removes the organic precursors of the by-products.

GENERAL DESCRIPTION

Ferric sulfate, $Fe_2(SO_4)_3$, is a yellow crystal or greyish-white powder that is soluble in water. In water treatment, it is usually supplied as an aqueous solution of 39–45% w/w ferric sulfate (11–12.5% Fe). The liquid solution has a specific gravity of 1.5–1.6 and is red-brown in colour. A 1% solution of ferric sulfate is acidic (pH 3–4).

Ferric sulfate is also available in granular form with an iron content of 18.5–20% and a pH of less than 1. It is not as corrosive as ferric chloride. Ferric sulfate can be stored or transported in stainless steels, lead, fibreglass, rubber-lined carbon steel, polyvinyl chloride, polyethylene or polypropylene.

Ferric sulfate can be used in a system built for alum dosing, whereas ferric chloride cannot.

CHEMISTRY

Ferric sulfate is produced by the oxidation of ferrous sulfate or by dissolving ferric oxide in sulfuric acid. In water, the ferric (iron III) ion hydrolyses and precipitates, to an extent that depends on pH and dosage. Iron precipitates formed are goethite, $HFeO_2$, and iron hydroxide, $Fe(OH)_3$, which are less soluble than aluminium precipitates. At equilibrium, the concentration of the soluble species is very low. Fe cations interact with the natural alkalinity to form hydroxides that then act in a charge neutralisation fashion similar to that for aluminium. Charge neutralisation destabilises the repulsive forces between the negatively charged particles, allowing them to approach closely, collide and agglomerate. Metal hydroxides precipitate and can enmesh any colloidal particles. Iron floc is generally large and settles rapidly though it may be weaker than alum floc. As for aluminium, sweep coagulation can also occur at higher doses.

The stoichiometry of the precipitation of iron hydroxides is described as follows:

$$Fe_2\,(SO_4)_3 \rightarrow 2Fe^{+3} + 3SO_4^{\;2-}$$

$$Fe^{+3} + 3OH^- \rightarrow Fe\,(OH)_3\,(s)$$

Ferric sulfate is an effective coagulant at pH values between 4 and 11.

TYPICAL USE IN DRINKING WATER TREATMENT

Ferric sulfate is used as a primary coagulant in the treatment of drinking water, particularly when a broad coagulation pH range is required.

The dose of ferric sulfate used depends on the properties of the raw water, including factors such as turbidity, natural organic matter (NOM), temperature and alkalinity.

Typical ferric sulfate doses, expressed as mg/L $Fe_2(SO_4)_3$, range from 2 mg/L to 100 mg/L although higher doses may be required if the raw water is excessively dirty. At high doses, product water should be tested to ensure that maximum contaminant levels have not been exceeded.

The dose rate of ferric sulfate may be expressed as crystalline ferric sulfate, as supplied liquid or as iron. Care should be taken when interpreting dose rates to ensure that any comparisons made are relevant.

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

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies depending on the manufacturing process. Chemical contaminants that may be present in ferric sulfate are (JECFA, KIWA 1994, NRC 1982):

- antimony
- arsenic
- cadmium
- chromium
- cobalt
- copper
- cyanide
- lead
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- titanium
- vanadium
- zinc

In some products, manganese concentrations may be high enough to affect the treated water.

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ferric sulfate 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*.

Almost all of the ferric ions used for coagulation are removed by optimised conventional water treatment processes. Residual sulfate is usually at low levels which do not adversely affect drinking water quality.

The presence of any ferrous iron in the product reduces its effectiveness in water treatment and increases the possibility of soluble iron carry over. Iron residuals after filtration can cause floc to form in the distribution system, which can give rise to customer complaints. To minimise residual levels of iron, pH and dosage conditions should exceed the solubility of iron. Poor dosage selection or inadequate mixing also leads to elevated iron residuals.

STATUS

Ferric sulfate 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

LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and* ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B406-97. AWWA CD-ROM (April 2003). Details at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

KIWA (1994) *Guideline quality of materials and chemicals for drinking water supplies*. Inspectorate of Public Health and Environmental Planning, Publication 94-01. Rijswijk, The Netherlands.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

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

Hydrochloric acid

(endorsed 2005)

Hydrochloric acid is used to correct pH, regenerate deionisers and generate chlorine dioxide on site.

GENERAL DESCRIPTION

Hydrochloric acid, HCl, also known as spirits of salts, is a colourless or slightly yellow, fuming, pungent liquid. This strong and highly corrosive acid should be handled with extreme caution (particularly when adding the concentrated acid to water), as it can cause severe burns and eye damage. Hydrochloric acid is generally available as a 25–42% solution. A 28% solution has a specific gravity of 1.14 at 20°C. The acid is soluble in water and benzene, and is noncombustible.

Hydrochloric acid is highly corrosive to most metals or alloys, liberating extremely flammable hydrogen gas. Chlorine gas may also be liberated in reactions with oxidants or sodium hypochlorite. Hydrochloric acid may be stored and piped in rubber-lined carbon steel, fibreglass-reinforced plastic with acid-resistant resins, plastic liners and pipes (u-polyvinyl chloride, polythene and polypropylene).

CHEMISTRY

Hydrochloric acid is manufactured by the combustion of chlorine gas in hydrogen to produce hydrogen chloride gas, which is then dissolved in water.

Hydrochloric acid disassociates in water to produce a strong acid:

$$HCl \Leftrightarrow H^+ + Cl^-$$

To reduce fuming, the acid should be diluted (by adding acid to water) to about 20% HCl.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, hydrochloric acid is used to correct pH (for softening, corrosion control, coagulation, prevention of post-precipitation), regenerate deionisers and generate the disinfectant chlorine dioxide on site.

Doses of hydrochloric acid required vary widely, depending on the application and conditions.

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 this product (JECFA, KIWA 1994):

- arsenic
- chlorine
- chromium
- iron
- lead
- lead
- methylene chloride
- nickel
- sulfate
- sulfur dioxide

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

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

When employed in drinking water treatment, hydrochloric acid 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*.

STATUS

Hydrochloric acid was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

Clesceri *Wastewater*, 20th edition. American Public Health Association, Washington, DC.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

KIWA (1994) *Guideline quality of materials and chemicals for drinking water supplies*. Inspectorate of Public Health and Environmental Planning, Publication 94-01. Rijswijk, The Netherlands.

Hydrofluorosilicic acid

(endorsed 2005)

Hydrofluorosilicic acid is used to artificially fluoridate water, to reduce the occurrence of dental caries. When dissolved in water, hydrofluorosilicic acid forms the fluoride ion⁻.

GENERAL DESCRIPTION

Hydrofluorosilicic acid, H_2SiF_6 (also known as fluorosilicic acid, hexafluorosilicic acid), is a colourless to pale yellow liquid, poisonous and corrosive, with a pungent odour and irritating fumes. It can etch glass. It has a specific gravity of 1.18 at 20°C at 22% strength.

The acid is usually delivered by road tanker but can be supplied in drums. It is incompatible with glass and stoneware but can be stored in polythene drums, rubber-lined mild steel or polyvinyl chloride-lined plastic tanks.

CHEMISTRY

Hydrofluorosilicic acid is a by-product of the preparation of chemical fertilisers from phosphate rock. The rock is ground up and treated with sulfuric acid, forming a gas by-product, which then reacts with water to produce a weak acid. This hydrofluorosilicic acid solution is subsequently concentrated to strengths of up to 30%. Manufacture of hydrofluorosilicic acid is limited, but because the acid is a by-product of the agricultural industry, it is generally readily available in Australia.

The dissolution of hydrofluorosilicic acid in water forms the fluoride ion (F^-) as follows:

$$H_2SiF_6 \Leftrightarrow 2H^+ + SiF_6^{2-}$$

$$SiF_6^{2-} \Leftrightarrow SiF_4 + 2F^-$$

$$SiF_4 + 2H_2O \Leftrightarrow SiO_2 + 4F^- + 4H^+$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Hydrofluorosilicic acid is used to fluoridate drinking water, to reduce the occurrence of dental caries. In each State and Territory, except for South Australia, the fluoridation of drinking water is regulated by an Act of Parliament; New South Wales and Queensland also have regulations in force.

In adding hydrofluorosilicic acid to drinking water, it is good practice to add the chemical after the water has been treated, because fluoride ions may be adsorbed onto the surfaces of suspended matter in water. In water that has been treated and disinfected, fluoridation is usually accomplished with a 20% hydrofluorosilicic acid stock solution. The acid solution, despite its pH of 1.2, has little effect on the pH of highly alkaline water, because relatively low amounts are used. However, the pH effect can be significant with water of low alkalinity.

The target levels of fluoride in fluoridated water in Australia vary between 0.7 and 1.0 mg/L. The lower concentrations apply in warmer climates, where more water is consumed. For an acid solution of 20% strength (15.8% F^-), this range translates to a dose of hydrofluorosilicic acid of 4.4–6.3 mg/L.

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

CONTAMINANTS

Chemical contaminants that may occur in hydrofluorosilicic acid solutions include inorganic and organic substances, and the following chemicals:

- arsenic
- lead

The concentrations of contaminants depend on the purity of the raw materials used in fertiliser production. Hydrofluorosilicic acid solutions also contain free hydrofluoric acid, which prevents the precipitation of solid silica when the acid is diluted in water.

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, hydrofluorosilicic acid 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*.

Fluoride forms precipitates with many metals and other elements, but is notably insoluble with calcium; thus, scaling can occur when concentrated lime solution and concentrated fluoride solution come into contact. Points for adding these solutions should be separated, to avoid this situation.

STATUS

Hydrofluorosilicic acid 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B703-00. AWWA CD-ROM (April 2003). Details at <www.awwa.org>

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Department of Health, South Africa (2003). *Water fluoridation, a manual for water plant operators.*

NSW Health (1957). Code of Practice for the fluoridation of public water supplies. *NSW Fluoridation of Water Supplies Act 1957*, NSW Government Gazette No. 135.

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

Hydrogen peroxide

(endorsed 2005)

Hydrogen peroxide is used as an oxidant in the treatment of drinking water (often in conjunction with ozone) to oxidise metals or organics, reduce tastes and odours, or act as an algicide, disinfectant or biocide. It can also be used to destroy ozone residual.

GENERAL DESCRIPTION

Hydrogen peroxide, H_2O_2, is a colourless syrupy liquid that is available in concentrations ranging from 20 to 60%, with a specific gravity between 1.07 and 1.24 at 20°C and pH 1–4.

There are strict handling and storage requirements that must be adhered to for hydrogen peroxide, which is especially dangerous at concentrations over 52%, because it is a strong oxidant and extremely corrosive. Materials suitable for handling and storing hydrogen peroxide include passivated aluminium or stainless steel (types 304L and 316L). Plastic piping (polyvinyl chloride or polyethylene) is only suitable for short-term use.

CHEMISTRY

Hydrogen peroxide is manufactured by electrolytic or organic auto-oxidation processes. A common example is the auto-oxidation of alkylated anthraquinones through hydrogenation with oxidation in the presence of a catalyst.

Used with ozone, hydrogen peroxide produces the powerful hydroxyl radical:

$$2H_2O_2 + 2O_3 = 4OH^{\bullet} + 3O_2$$

For the destruction of ozone in water, this reaction proceeds to water and oxygen.

Hydrogen sulfide, a common taste and odour compound, is oxidised to sulfate by hydrogen peroxide as follows, or to colloidal sulfur.

$$4H_2O_2 + H_2S \Leftrightarrow SO_4^{2-} + 4H_2O + 2H^+ \qquad \text{pH} > 8$$

$$H_2O_2 + H_2S \Leftrightarrow S + 2H_2O \qquad \text{pH } 7$$

Hydrogen peroxide also oxidises iron and manganese, which are then precipitated.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In water treatment, hydrogen peroxide is used with ozone to produce the hydroxyl radical, which is a powerful oxidant. The combination of hydrogen peroxide and ozone is used to:

- oxidise iron, manganese, sulfide and hazardous synthetic organic compounds such as trichloroethylene and atrazine
- remove taste and odour-causing substances, such as hydrogen sulfide (H_2S) which is commonly found in groundwater
- reduce colour and natural organic matter
- improve the performance of coagulants, or reduce the required amount of coagulants.

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

Hydrogen peroxide is a biocide, and can be used before treatment to control the growth of aquatic organisms such as algae in the pre-treatment basin. It may also be used as a primary disinfectant to meet the C.*t* (disinfectant concentration × contact time) requirements. Alternatively, hydrogen peroxide can be used after the ozonation stage to destroy ozone residual and minimise its release to the atmosphere.

Hydrogen peroxide is often added at the head of a treatment plant, before or at the rapid mix basin. However, it can also be added after clarification and before filtration, when a substantial portion of the oxidant demand has been removed.

To determine the optimum hydrogen peroxide concentration for a particular application, it is best to undertake pilot-plant and jar-testing trials. For use with ozone, the hydrogen peroxide to ozone ratio is typically 0.4–0.5; whereas, for destroying ozone residual, a concentration of 1.4 mg/L of H_2O_2 (50% strength) would be required for each mg/L of ozone.

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 hydrogen peroxide (JECFA):

- acetanilide
- acetophenetidin
- arsenic
- copper
- iron
- sulfuric acid
- tin

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

Hydrogen peroxide decomposes to oxygen and water.

When employed in drinking water treatment, hydrogen peroxide 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*.

STATUS

Hydrogen peroxide 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

IARC (International Agency for Research on Cancer) (1999). *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*. World Health Organization, Geneva, 71: 683.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

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White GC (1992). *Handbook of chlorination and alternative disinfectants*, 3rd edition. Van Nostrand Reinhold, New York.]

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

Hydroxylated ferric sulfate

(endorsed 2005)

Hydroxylated ferric sulfate is used as a coagulant for the treatment of drinking water. It is effective over a broad pH range and generally produces a stronger floc than other ferric salts.

GENERAL DESCRIPTION

Hydroxylated ferric sulfate (HFS), $Fe_x(SO_4)_y(OH)$, also known as polymerised ferric sulfate, is one of several hydroxylated iron coagulants produced from ferrous sulfate. It is a translucent, dark reddish liquid, with no odour. It is available in various ferric iron and basicity concentrations, but typically contains 12.5 % Fe.

HFS has a pH of less than 2 and a specific gravity of 1.45–1.6 at 25°C. It is corrosive, but can be stored in fibreglass, rubber-lined steel, stainless steel, polyethylene, polyvinyl chloride or polytetrafluoroethylene.

For commercial coagulant solutions, the basicity varies from about 5 to 15% for prehydrolysed iron salts. As the basicity exceeds 15%, it becomes increasingly difficult to keep the metal hydroxide precipitate from forming in the product solution during shipping and extended storage. The typical basicity for HFS is 10%.

CHEMISTRY

HFS is produced by oxidising ferrous sulfate. It can also be produced by dissolving ferrous oxide in sulfuric acid under controlled conditions. The chemical is similar to ferric sulfate, but its small polymeric chains provide additional coagulation properties, so it may be preferable to ferric sulfate for water that is difficult to treat.

In water, ferric (iron III) ion hydrolyses and precipitates, to an extent that depends on pH and dosage. Iron precipitates formed are goethite (HFeO2) and iron hydroxide ($Fe(OH)_3$), which are less soluble than aluminium precipitates. At equilibrium, the concentration of the soluble species is very low. The stoichiometry of the precipitation of iron hydroxide is described as follows:

$$Fe^{+3} + 3OH^{-} \rightarrow Fe\ (OH)_3\ (s)$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

HFS coagulates relatively quickly over a wide pH range (pH 4–11). It forms a dense floc and does not cause significant variation in pH. The floc produced is usually similar in characteristics to alum floc, but has less impact on pH and alkalinity. HFS generally produces a more robust floc than other iron salts. It is often preferred over conventional coagulants for low alkalinity waters containing colour because it does not consume as much alkalinity as other coagulants; thus, the need to add alkali in addition to coagulant is reduced.

The dose of HFS used depends on the properties of the raw water, including factors such as turbidity, natural organic matter, temperature and alkalinity. As with other coagulants, higher doses are required as turbidity and colour increase, and colder temperatures slow down reaction times.

Typical HFS doses (expressed as supplied HFS in mg/L) are 5–100 mg/L, although higher doses may be required if the water is particularly dirty. At high doses, product water should be tested to ensure that maximum contaminant levels have not been exceeded.

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

The dose rate of HFS may be expressed as ferric sulfate, supplied HFS liquid or iron. Care should be taken when interpreting dose rates to ensure that relevant comparisons are made. Because of its reactivity, HFS should be used neat if possible, or not pre-diluted such that is hydrolyses before contact with the water to be treated.

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 HFS:

- antimony
- arsenic
- cadmium
- chromium
- cobalt
- copper
- cyanide
- lead
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- titanium
- vanadium
- zinc

In some products, manganese concentrations may be significant.

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, HFS 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*.

Almost all ferric ions used for coagulation are removed by conventional water treatment processes. Residual sulfate is usually at low levels that do not adversely affect drinking water quality.

STATUS

HFS was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). Standard Methods for the Examination of Water and Wastewater, 20th edition. American Public Health Association, Washington, DC.

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

Ozone

(endorsed 2005)

Ozone is used as an oxidant and disinfectant in the treatment of drinking water. It can oxidise metals and organic compounds, including algal toxins, tastes and odours. Ozonation does not produce a residual so cannot be used to maintain a disinfection residual in the distribution system.

GENERAL DESCRIPTION

Ozone (O_3) is an unstable blue or colourless gas with a pungent odour. It can be liquefied at –12°C, and has a boiling point of –112°C and a freezing point of –192°C. It is more soluble in water than oxygen. As a strong oxidant and disinfectant, ozone effectively inactivates bacteria, viruses and protozoa (*Cryptosporidium* and *Giardia*), controls tastes and odours, and breaks down organic contaminants and algal toxins. Ozone also aids in coagulation and flocculation, by breaking down organic chains and starting microflocculation. Ozone does not produce halogenated disinfection by-products, except in bromide-rich waters where bromate ion is generated.

Disadvantages of ozone are that it is relatively costly and does not produce a persistent disinfectant residual (and therefore cannot be used to maintain a disinfection residual in the distribution system).

Also, ozone produces biodegradable organic material that increases biofouling problems in the water distribution system. This biodegradable material can be achieved by using biologically activated carbon (BAC) filters after ozone treatment.

Ozone in water is highly corrosive; therefore, only it can only be used with certain materials, such as 316 and 305 stainless steel, glass and Teflon. Ozone is produced on site using electrical discharges in the presence of oxygen. The maximum concentration of ozone generated is 50 g/m^3 and the maximum practical solubility of ozone in water is approximately 40 mg/L.

CHEMISTRY

Ozone is produced on site, as described above, and is highly unstable in the gaseous phase. Ozone has a half-life of 20–100 hours in clean vessels, at room temperature.

Two types of reactions occur when ozone is added to water:

- direct oxidation (a slow and extremely selective reaction favoured by low pH conditions)
- auto-decomposition to the hydroxyl radical (a reaction catalysed by hydroxyl radicals, organic radicals, hydrogen peroxide, ultraviolet light or high concentrations of hydroxide ion; and favoured by high pH conditions or high concentrations of organic matter).

Ozone breaks down more slowly in water that has a high concentration of bicarbonate or carbonate. Therefore, an ozone residual will last longer in highly buffered water with low pH.

The reaction of ozone with contaminants in the water requires a sufficient contact time and a high transfer efficiency coefficient, which can be provided by well-designed ozone contactors and mixing devices. The gas vented from the contactors contains ozone, which has to be destroyed or re-injected before the air is released to the atmosphere.

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

TYPICAL VALUES USED IN AUSTRALIAN DRINKING WATER TREATMENT

Ozone is a very strong oxidant that is moderately soluble in water. Typical concentrations used in drinking water are 0.5–5 mg (O_3)/L, depending on the organic content of the water. The required dose should be determined through bench-scale ozone demand tests or pilot-plant testing, using available C.*t* (concentration × contact time) data for the inactivation of various microorganisms. The contact time required for ozone inactivation of microorganisms varies from seconds to minutes (the longer time being required for inactivation of protozoan cysts) and is temperature dependent; it is significantly shorter than the contact time required for chlorine or chloramines.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process and impurities in the air or oxygen used to generate the ozone. The following chemicals may be present in ozone:

- acetylene
- argon
- carbon dioxide
- carbon monoxide
- hydrocarbons
- nitrous oxide

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, ozone 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*.

Ozone can react with bromide to form brominated ozone, which includes bromate ion (BrO_3^-). If natural organic material is present, nonhalogenated organic disinfection by-products are formed. These include aldehydes (formaldehyde being dominant), ketoacids and carboxylic acids. If both natural organic material and bromide are present, hypobromous acid is formed, together with brominated organohalogen compounds.

STATUS

Ozone was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

APHA (1998). APHA 4500-O3, Ozone (residual), in Standard Methods for the Examination of Water and Wastewater, 20th Edition, American Public Health Association, Washington, DC.

Water Treatment Plant Design (1990). American Water Works Association, 3rd Ed. McGraw-Hill Companies, Inc.

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

Polyacrylamide

(endorsed 2005)

Polyacrylamide is used in water treatment as an aid to coagulation, flocculation, clarification, filtration or handling of sludge.

GENERAL DESCRIPTION

Polyacrylamide, $(CH_2CHCONH_2)_n$, is a white crystalline solid. It is hydrophilic, with molecular weights of 1–30 million daltons, and chain lengths of 1.4×10^4 to 4.2×10^5 monomer units. Polyacrylamide is available in anionic, cationic or non-ionic forms, and in a variety of molecular weights and charge densities, to suit the particular characteristics of the water to be treated. It may be supplied as a powder, as an aqueous solution, dispersed in a light mineral oil or bound up in a solid cake that slowly dissolves when immersed.

Appropriate handling materials for polyacrylamide include fibreglass-reinforced plastic, polyethylene, polypropylene, polyvinyl chloride, stainless steel and coated steel.

CHEMISTRY

Polyacrylamide is usually manufactured by the polymerisation of the acrylamide monomer (AM) to form a non-ionic polymer, polymerisation of AM with acrylic acid salts to form an anionic polymer, or polymerisation of AM with cationic monomer to form a cationic polymer.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, polyacrylamide may be added:

- as a coagulation aid, immediately after coagulation, to strengthen the precipitate formed
- as a flocculation aid, at the start of flocculation, to increase the agglomeration of the floc
- as a clarification aid, before clarification, to help settle floc, bind dissolved air bubbles to floc (in dissolved air flotation, DAF) or bind floc to microsand
- as a filtration aid, before filtration, to minimise floc shearing and to improve adsorption of floc onto the filter medium
- to backwash water, to minimise filter ripening periods
- to sludge for thickening or dewatering, to improve performance.

As a coagulation, flocculation or clarification aid, polyacrylamide is typically used at concentrations of 0.05–0.3 mg/L. As a filter aid, it is usually applied in lower doses (0.01–0.1 mg/L). For sludge handling, typical doses of polyacrylamide are 0.5–2 kg per tonne of dry solids for thickening, and 1–4 kg for dewatering.

High doses of polyacrylamide can cause clogging and blockages, particularly in filter beds. Therefore, where high doses of polymers are used in water treatment, it is best to clean filters by both air scouring and water washing. Even with relatively low doses of polyacrylamide, filter beds should be inspected regularly for signs of polymer build-up. Regular measurement of the headloss accumulation rate in a filter is also useful.

Care should be taken in making up polymer solutions to minimise the formation of lumps of undissolved polymer (referred to as 'fish eyes'). The polymer should be mixed with the water using a well-designed eductor, so that each grain of polymer is separately introduced to the water.

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

The polymer solution should also be suitably aged before dosing to obtain best performance. Aging requires gentle mixing of the polymer solution for 1–4 hours (refer to manufacturer for specific polymer aging times).

While most polymers are at least chlorine resistant, making up polymer solutions with chlorinated water can reduce their effectiveness.

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 this product, depending on the raw materials used:

- acetamide
- acetone
- acrylamide
- acrylic acid
- acrylonitrile
- copper
- hydroquinone
- methacrylamide
- methyl ether hydroquinone
- peroxide
- propanamide
- sulfate

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

Polyacrylamides contain varying residual amounts of unreacted acrylamide monomer.

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

STATUS

Polyacrylamide, acrylic acid polymers and copolymers were endorsed by the NHMRC as drinking water treatment chemicals in 1977 and 1979. The revision undertaken in 2003 did not result in any change to the status of this chemical for the treatment of drinking water.

REFERENCES

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B453-01. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Brown L and Rhead MM (1979). Liquid chromatographic determination of acrylamide monomer in natural and polluted aqueous environments. *Analyst* 104:391–399.

Letterman RD and Pero (1990). Contaminants in Polyelectrolyets used in Water Treatment. *American Water Works Association* 82(11): 87–97.

NICNAS (National Industrial Chemicals Notification and Assessment Scheme) (2002). *Priority Existing Chemical Assessment No 23: Acrylamide*, NICNAS, Canberra.

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

Polyaluminium chloride

(endorsed 2005)

Polyaluminium chloride is used as a primary coagulant in the treatment of drinking water. It is effective over a range of pH values. It is particularly effective on some waters and usually requires a lower dose than alum.

GENERAL DESCRIPTION

Polyaluminium chloride (PACl), $Al_2(OH)_3Cl_3$, is also known as aluminium hydroxy chloride or basic aluminium chloride. In solution, PACl is colourless to pale yellow, clear to slightly cloudy liquid. It is usually supplied with a minimum of 10% Al_2O_3 content, a pH of 2.2–2.8 and a basicity of about 50% (w/w). PACl solution has a specific gravity of 1.18–1.22 at 20°C and is completely soluble in water. Its use requires less alkalinity adjustment than most coagulants because of its basicity.

The formula $Al_2(OH)_3Cl_3$, is simply a representation of the proportions of aluminium, hydroxide and chloride in the solution. A generic formula for the PACl species may be given as $Al_2(OH)_mCl_{(6-m)}$ where the value of m typically ranges from 2.5 to 3.5.

PACl can be stored in fibreglass or plastics (polyethylene, polypropylene or polyfluorene), but is corrosive to most materials, including stainless steel (although 316 stainless steel can be used).

CHEMISTRY

PACl is manufactured by the reaction of hydrochloric acid with aluminium-containing raw materials such as aluminium metal, alumina trihydrate, aluminium chloride or aluminium sulfate.

PACl solution is a complex, dynamic mixture of positively charged polynuclear aluminium species, with no single species predominating. When applied to water, these species interact with and destablise negatively charged colloidal matter, such as inorganic particles and the high molecular weight organic compounds that largely constitute natural organic matter. The polynuclear species also hydrolyse to form dense flocs of aluminium hydroxides that further act to entrap particles and remove some organic.

An example of one of the many polynuclear species that may be present in PACl solution is the so called Al-13 ion that has the formula $[AlO_4.Al_{12}(OH)_{24}(H_2O)_{12}]^{13+}$.

The hydrolysis of PACl produces less acid than the hydrolysis of aluminium sulfate owing to the high degree of hydroxylation of the aluminium. As a result, PACl generally requires less pH correction with alkali than if alum were the coagulant.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

PACl is used as a primary coagulant to reduce turbidity, metals, colour and natural organic matter.

The amount of PACl added as a coagulant depends on the properties of the raw water, including factors such as turbidity, dissolved organic carbon, temperature and alkalinity.

Typical PACl doses (with 10% Al_2O_3 content) are 5–100 mg/L, although higher doses can be required if the water is particularly dirty. Doses should be determined by laboratory trials.

PACl is the next most commonly used aluminium salt after alum. Compared to alum, it produces a relatively robust floc, generally requires lower doses and is effective over a wider pH range.

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

CONTAMINANTS

PACl solution is usually low in trace metals, because it is made from clean raw materials. However, the following chemical contaminants may be present in this product:

- antimony
- arsenic
- barium
- beryllium
- cadmium
- chromium
- copper
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- thallium
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, PACl 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*.

Most of the aluminium ions resulting from the use of PACl as a coagulant are removed by conventional water treatment processes. Residual chloride will be present, but at low levels that do not adversely affect drinking water quality.

STATUS

Polyaluminum chloride was endorsed by the NHMRC for use as a drinking water treatment chemical in 1979. The revision undertaken in 2003 did not change the status of this chemical for the treatment of drinking water.

REFERENCES

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B408-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. American Public Health Association, Washington, DC.

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

Polyaluminium silica sulfates

(endorsed 2005)

Polyaluminium silica sulfates are a relatively new group of coagulants in the treatment of drinking water. They are effective for removal of metals, colour and turbidity, and readily forms floc even in clean water.

GENERAL DESCRIPTION

Polyaluminium silicate sulfate, $Al_A(OH)_B(SO_4)_C(SiO_x)_D{\cdot}E(H_2O)$ (also known as aluminium hydroxide silicate sulfate) are pale yellow in colour and appears slightly cloudy to clear. It is usually supplied with a minimum of 9.8% Al_2O_3, a basicity of about 54% and a specific gravity of 1.32–1.36 (at 25°C). It has a pH of 2.8–3.6. It can be stored in fibreglass, plastics and stainless steel.

CHEMISTRY

Polyaluminium silicate sulfate is manufactured from alum, soda ash, sodium silicate and sodium aluminate.

Polyaluminium silicate sulfate solution is a polymerised coagulant solution containing aluminium in short chains. The high basicity of polyaluminium silicate sulfate assists in flocculation, because the coagulant does not require alkalinity to form the initial floc. The charge on colloidal particles and dissolved organics is neutralised by adsorption onto the very small flocs that form initially. Silicate compounds in polyaluminium silica sulfate help to form larger flocs faster than with many other coagulants.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Polyaluminium silicate sulfate is used as a coagulant in the treatment of water and wastewater and to assist sludge blanket formation at start up. Polyaluminium silicate sulfate forms floc rapidly, even in cold water. It tends to form floc even with clean dilution water; therefore, it should be added as supplied (i.e. undiluted).

Typical concentrations of polyaluminium silicate sulfate used in drinking water treatment depend on the quality of the water to be treated and the purpose of the treatment. Polyaluminium silicate sulfate doses are typically 5–100 mg/L, but may be higher if the water is particularly dirty. The appropriate concentration should be determined by laboratory trials. Polyaluminium silicate sulfate must be used undiluted in jar tests.

CONTAMINANTS

The following contaminants may be present depending on the manufacturing process:

- antimony
- arsenic
- barium
- beryllium
- cadmium
- chromium
- copper
- fluoride
- iron
- lead
- magnesium
- manganese
- mercury
- nickel
- phosphorus
- selenium
- silver
- thallium
- zinc

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

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, polyaluminium silicate sulfate 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*.

STATUS

Polyaluminium silicate sulfate was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Clifford DA (1999). Ion Exchange and Inorganic Adsorption. In: *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed), American Water Works Association, 5th edition. McGraw-Hill Professional, New York, 9.1–9.91.

Lewis RJ Sr (1993). *Hawley's Condensed Chemical Dictionary*, 12th edition. Van Nostrand Reinhold, New York.

McGregor S (2002) Pass for P.A.S.S. on OHS and treatment. WaterWorks, December pp 12-15.

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

Polydiallyldimethylammonium chloride

(endorsed 2005)

Polydiallyldimethylammonium chloride (polyDADMAC) is used in the treatment of drinking water as a primary coagulant or, together with an inorganic coagulant, as a coagulation aid. PolyDADMAC reduces the quantities of floc and sludge produced.

GENERAL DESCRIPTION

Polydiallyldimethylammonium chloride $(C_8H_{16}N{\cdot}Cl)_n$, (also known as polyDADMAC), is a cationic polyelectrolyte with a medium molecular weight range of 105–106 and a high charge density (50–100%). The chemical is available as a powder or aqueous solution (10–60%). PolyDADMAC is not pH sensitive and is chlorine resistant.

Appropriate handling materials for polyDADMAC include fibreglass-reinforced plastic, polyethylene, polypropylene, polyvinyl chloride, stainless steel and coated steel.

CHEMISTRY

PolyDADMAC is produced from the diallyldimethylammonium chloride (DADMAC) monomer, which is made from allyl chloride and dimethylamine.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

PolyDADMAC can be used in a conventional treatment process as a primary coagulant for neutralisation and precipitation, in place of metal salts. The positively charged polyDADMAC reacts with turbidity particles and humic substances, which are generally negatively charged. The reaction eliminates the charge, allowing the particles to agglomerate. PolyDADMAC is usually most effective with particulate material; it may be less useful than aluminium and iron salts for treating dilute inorganic suspensions and water with significant amounts of colour.

PolyDADMAC can also be used as a secondary coagulant, to partially replace inorganic salts. A small dose of polyDADMAC may significantly reduce the amount of inorganic salt required (thus reducing floc volume and improving filter run times); often, it also improves treated water quality. PolyDADMAC is used particularly in direct and contact filtration processes, where the objective of coagulation is to produce small, high-density aggregates.

In treatment of drinking water, typical concentrations of polyDADMAC are 0.2–6 mg/L (as 100% polyDADMAC). When polyDADMAC is used, together with an inorganic salt, as a secondary coagulant, concentrations are usually lower (0.2–1 mg/L). The amount of polyDADMAC required should be determined through jar testing. The chemical can be added at concentrations of up to 10 mg/L, provided that the residual concentration of the monomer (DADMAC) does not exceed 2% of the polymer, and that the concentration of the residual monomer does not exceed 0.2 mg/L in the clarified water.

At concentrations above 40%, polyDADMAC is difficult to pump, because of its relatively high viscosity. Excessive polymer concentrations can adversely affect coagulation and filtration by re-dispersing the impurities.

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

Being highly charged, polyDADMAC should be diluted before it is added to the main water stream, so that it mixes more easily.

PolyDADMAC is usually supplied as a liquid. If supplied as a solid, individuals should seek advice from the supplier of the polymer as how to best prepare it.

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 this product:

- 5-hexenal
- allyl chloride
- DAD monomers
- beryllium
- cadmium
- chromium
- copper
- fluoride
- iron
- lead
- diallyl ether
- dimethylamine
- mercury
- nickel
- phosphorus
- selenium
- silver
- thallium
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, polyDADMAC 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*.

Diallyldimethylammonium chloride residues are present in polyDADMAC.

STATUS

PolyDADMAC was endorsed by the NHMRC for use as a drinking water treatment chemical in 1982. The revision undertaken in 2003 did not change the status of this chemical for the treatment of drinking water.

REFERENCES

NSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B451-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Bolto, B. (August, 1994). Polymeric Flocculants in Water Purification. *Water Chemistry Supplement* in *Water Journal* 21(4): 431-433.

Letterman RD and Pero (1990). Contaminants in Polyelectrolytes used in Water Treatment. *American Water Works Association* 82(11): 87–97.

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

Potassium permanganate

(endorsed 2005)

Potassium permanganate is mainly used for the oxidation and removal of iron and manganese; it can also be used as a disinfectant, or to control tastes and odours.

GENERAL DESCRIPTION

Potassium permanganate, $KMnO_4$, is a dark purple crystal with a blue metallic sheen. It has a sweetish, astringent taste, is odourless and is an oxidant. The chemical is commercially available in crystalline form. Potassium permanganate is highly soluble in water, but heating is usually needed to prepare solutions with concentrations of more than 2.5%.

Appropriate handling materials include iron, steel, stainless steel, fibreglass-reinforced plastic, polyethylene and polyvinyl chloride.

CHEMISTRY

Potassium permanganate is produced by fusing manganese dioxide with potassium hydroxide to form potassium manganate; a solution of the manganate is then electrolysed at about 60°C using iron electrodes.

Under most treatment applications, permanganate (MnO_4^-) is reduced to insoluble manganese dioxide (MnO_2 (s)).

Divalent manganese (Mn^{2+}) is removed from water by the oxidation to insoluble manganese dioxide (MnO_2). As the oxidant, the permanganate ion MnO_4^- is itself reduced to manganese dioxide. The reaction proceeds as follows:

$$3Mn^{2+} + 2MnO_4^- + 4OH \rightarrow 5MnO_2 + 2H_2O$$

The stoichiometric ratio of $KMnO_4$ to soluble Mn^{2+} is 1.92:1; however, reactions with organics usually require significantly higher ratios. The alkalinity consumed is 1.2 mg of CaCO3 per milligram of Mn^{2+}, and the sludge produced (based on MnO_2 as the precipitate) is 2.6 kg/kg Mn^{2+}.

Potassium permanganate can also be used to oxidise iron and organics. The stoichiometric ratio of $KMnO_4$ to soluble Fe^{2+} is 0.94:1; however, reactions with organics usually require higher ratios. The alkalinity consumed is 1.5 mg per mg of Fe^{2+} and the sludge produced (based on $Fe(OH)_3$ as the precipitate) is 2.4 kg/kg Mn^{2+}.

Manganese dioxide resulting from permanganate reduction is an effective adsorbent for ferrous iron (Fe^{2+}), manganous manganese (Mn^{2+}), radium (Ra^{2+}) and other trace inorganic cationic species. These contaminants can be removed by permanganate treatment.

Manganese dioxide also adsorbs natural organic materials that serve as precursors for disinfection by-products. This characteristic of manganese dioxide is particularly pronounced in hard waters, presumably because of the bridging action of calcium and manganese.

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

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, potassium permanganate can be fed into solution directly using a dry chemical feeder or as a liquid bulk supply using dosing pumps. Alternatively, a concentrated solution can be prepared on site, from which the desired concentration is added to the water.

Permanganate is often added at the head of the treatment plant, as close to the intake as possible. This allows sufficient time for the permanganate to perform its oxidative function and to be reduced completely to solid manganese dioxide before filtration. In some cases, an alkali (usually lime) is added before, or soon after, addition of potassium permanganate, to assist in the oxidation process. Potassium permanganate can be effective over a range of pH values, but is most effective at pH 8.5 or higher.

The adsorptive property of MnO_2(s) is the principle underlying the historical manganese greensand process, in which the filter medium is coated with manganese dioxide, which subsequently serves as an adsorbent for Fe^{2+}, Mn^{2+} and other metals in the filter influent. Filter media can be coated with manganese oxide by applying a potassium permanganate solution to the filter bed and oxidising it (through chlorination or aeration). Low doses of chlorine or permanganate are applied to the filter influent to catalyse the oxidation of the adsorbed metals, thereby creating additional adsorption sites. Alternatively, the filter backwash water may be treated with chlorine or permanganate.

Concentrations of potassium permanganate used in drinking water treatment depend on the concentrations of metals and organics, but are usually 0.3–5 mg/L. Overdosing of the chemical should be avoided because of the pink colour of unreacted permanganate. The potassium permanganate levels required should be determined by jar testing.

Advantages of potassium permanganate include its ease of use and the fact that it is effective for the oxidation of both iron and manganese and for certain types of taste and odour. As a disinfectant, it produces no halogenated disinfection by-products, but has only a limited disinfection capability.

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 this product (NRC 1982):

- cadmium
- chloride
- chromium
- mercury
- sulfate

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, potassium permanganate 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 manganese dioxide produced is a black precipitate that can be removed by a conventional clarification or filtration process. If manganese dioxide is not properly removed, the precipitates will create particulate deposits in the distribution system and on household plumbing fixtures. At manganese concentrations above 0.02 mg/L, an increase in consumer complaints is common.

STATUS

Potassium permanganate 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.

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

REFERENCES

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B603-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

White GC (1992). *Handbook of chlorination and alternative disinfectants*, 3rd edition. Van Nostrand Reinhold, New York.

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

Sodium aluminate

(endorsed 2005)

Sodium aluminate is used as a primary coagulant in drinking water treatment, especially in water with low alkalinity; it can also be used in combination with alum to control alkalinity and pH.

GENERAL DESCRIPTION

Sodium aluminate, $Na_2Al_2O_4$, is a white powder that is hygroscopic, soluble in water and strongly alkaline. The aqueous solution is a clear, colourless to pale amber liquid, with a pH of 14.

Sodium aluminate can be supplied as a powder or as a solution. The solid product contains 70–90% $Na_2Al_2O_4$, whereas the liquid form contains 29–35% $Na_2Al_2O_4$. The liquid solution has a specific gravity of 1.4–1.6, with an excess alkali (as sodium hydroxide, NaOH) of 8–13% and Al_2O_3 equivalent of 18–21%.

Appropriate handling materials for sodium aluminate include iron, fibreglass-reinforced plastic, polyethylene, rubber, steel, stainless steel and concrete.

CHEMISTRY

Sodium aluminate is produced by combining aluminium oxide with excess caustic soda.

The aluminium ion neutralises the negative charges on turbidity particles and also forms insoluble metal hydroxides that agglomerate the neutralised particles:

$$Na_2Al_2O_4 + 4H_2O \rightarrow 2Na^+ + 2Al^{+3} + 8OH^-$$

$$Al_2O_3 + 3H_2O \Leftrightarrow 2Al(OH)_3(s)$$

1 mg/L of $Na_2Al_2O_4$ (88%) increases the alkalinity of the water by 0.54 mg/L and reduces carbon dioxide, CO_2, by 0.47 mg/L.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sodium aluminate is used as a primary coagulant, especially in water with low alkalinity. It can also be used in combination with alum to control alkalinity and pH. An advantage of sodium aluminate is that the chemical provides both aluminium and alkali. However, its use as a coagulant in water treatment is limited by cost and by its chemical properties, which make it more difficult to handle than alum or other metal salts.

Because sodium aluminate contains a high percentage of aluminium, a concentration of 1 mg/L of $Na_2Al_2O_4$ is equivalent to 3.5 mg/L of alum (on a dry weight basis).

Typical concentrations used are 2–60 mg/L (as $Na_2Al_2O_4$). The appropriate level should be determined by jar testing.

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

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 this product:

- arsenic
- cadmium
- chromium
- iron
- lead
- mercury
- selenium
- silver

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium aluminate 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*.

Aluminium residuals remaining after filtration can cause floc to form in the distribution system, which can lead to customer complaints.

STATUS

Sodium aluminate 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

NSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B405-00. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

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

Sodium bicarbonate

(endorsed 2005)

Sodium bicarbonate is used to correct pH, control corrosion, soften water for coagulation and prevent post-precipitation.

GENERAL DESCRIPTION

Sodium bicarbonate, $NaHCO_3$ (also known as baking soda, bicarbonate of soda, sodium acid carbonate or sodium hydrogen carbonate), is in the form of a white powder or crystalline lumps, and has a slightly alkaline taste. It is soluble in water (96 g/L at 20°C) and stable in dry air, but slowly decomposes in moist air. Its specific gravity is 2.159 at 20°C, with a bulk density of 1000 kg/m^3. Sodium bicarbonate is available in several grades, but is usually supplied as > 99% sodium bicarbonate. A 10 g/L solution has a pH of 8.4. The chemical decomposes with heat (> 50°C) and reacts with acid to release carbon dioxide.

Suitable storage materials for sodium bicarbonate include rubber linings and stainless steel.

CHEMISTRY

Sodium bicarbonate is most economically produced by bubbling carbon dioxide gas through a solution of purified sodium carbonate; the bicarbonate precipitates out and can be collected and dried. Sodium bicarbonate is also an intermediate product in the Solvay process for making sodium carbonate.

Sodium bicarbonate provides bicarbonate alkalinity without significantly changing the pH of the water:

$$NaHCO_3 \Leftrightarrow Na^+ + HCO_3^-$$

It can further break down to carbon dioxide in the presence of acid:

$$HCO_3^- + H^+ \Leftrightarrow CO_2 + H_2O$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sodium bicarbonate is used to correct pH, control corrosion, soften water for coagulation and prevent post-precipitation. It is used as a source of alkalinity for the treatment of waters with low alkalinity, but is more expensive than soda ash or lime. When it is used to improve coagulation, additional alkalinity or pH adjustment is often required.

The concentration of sodium bicarbonate required depends on the alkalinity and pH of the raw water and the targets for the treated water. Jar testing should be used to determine requirements.

Sodium bicarbonate can increase alkalinity with little increase in pH. It imparts a change of 0.60 g/L $CaCO_3$ alkalinity per mg/L as $NaHCO_3$.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water will vary depending on the manufacturing process. The following chemical contaminants may be present in this product (JECFA):

- ammonium
- arsenic
- chloride
- iron

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

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

When employed in drinking water treatment, sodium bicarbonate 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*.

Sodium, alkalinity, carbonate and carbon dioxide are the only significant residues that are expected to occur from sodium bicarbonate, but none of these is likely to become a problem at normal doses.

STATUS

Sodium bicarbonate 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

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

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

DRINKING WATER TREATMENT CHEMICALS –
FACT SHEETS

Sodium carbonate

(endorsed 2005)

Sodium carbonate is used to correct pH, control corrosion, soften water for coagulation and prevent post-precipitation.

GENERAL DESCRIPTION

Sodium carbonate, Na_2CO_3 (also known as soda ash), is a hygroscopic, greyish-white powder. It is supplied in the form of crystalline granules containing more than 99% sodium carbonate. It is soluble in water (to 250 g/L) and noncombustible. The chemical is available in different grades. Dense soda ash (specific gravity 2.15, bulk density 1000 kg/m^3) is most commonly employed in the water industry, but light soda ash (specific gravity 2.53, bulk density 500 kg/m^3) may also be used. Liquid soda ash is also available as a solution of various concentrations. Liquid soda ash is typically supplied as a 10 % w/v solution that has a specific gravity of 1.1(25°C) and a pH of up to 12.5. A 1% solution has a pH of 11.3.

Appropriate materials for handling sodium carbonate include rubber linings, iron, steel, fibreglass reinforced plastic and polyethylene.

CHEMISTRY

Sodium carbonate is found in natural deposits and is mined. It is also recovered, with other chemicals, from lake brines. However, most is produced through the Solvay process, in which ammonia and carbon dioxide are passed into a saturated sodium chloride solution, forming first ammonium hydrogen carbonate, then soluble ammonium chloride and a precipitate of sodium hydrogen carbonate (sodium bicarbonate). The precipitate is filtered off and heated to produce sodium carbonate.

Sodium carbonate produces hydroxide and bicarbonate ions in water:

$$Na_2CO_3 + H_2O \Leftrightarrow 2Na^+ + HCO_3^- + OH^-$$

Sodium carbonate is used together with lime to remove noncarbonate hardness (that portion of calcium and magnesium present as noncarbonate salts) as shown below:

$$MgSO_4 + Ca(OH)_2 \Leftrightarrow Mg(OH)_2 + CaSO_4$$

$$CaSO_4 + Na_2CO3 \Leftrightarrow CaCO_3 + Na_2SO_4$$

The solubility of magnesium hydroxide varies with pH. A pH of 11–11.3 is usually needed to remove magnesium effectively; this will require a concentration of lime higher than the stoichiometric requirement.

The quantity of sodium carbonate needed to remove noncarbonate hardness can be estimated using the following equation:

$$Na_2(CO)_3 \text{ (mg/L)} = 1.05 \text{ x (noncarbonate hardness removed (mg/L))}$$

Noncarbonate hardness is expressed as $CaCO_3$.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sodium carbonate is used mainly as a source of alkalinity and pH adjustment. It is more expensive than lime but is generally easier to handle, because of its higher solubility. If hard water is used for making up or diluting a solution of sodium carbonate, calcium carbonate may precipitate. This reduces the strength of the solution and can produce scale in the delivery pipelines. In this situation, the service water supplied to the soda ash system needs to be softened.

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

Sodium carbonate is usually made up as a solution of up to 20% concentration. Concentrations of sodium carbonate used in drinking water treatment depend on the quality of the water to be treated and the purpose of the treatment (water softening, pH adjustment or alkalinity increase). Based on stoichiometry, 1 mg/L of sodium carbonate provides alkalinity equivalent to about 0.7 mg/L of hydrated lime. Typical sodium carbonate concentrations used can vary from 5 to more than 500 mg/L, and the appropriate concentration should be determined by laboratory trials.

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 sodium carbonate (JECFA, KIWA 1994, NRC 1982):

- arsenic
- cadmium
- calcium
- chloride
- chromium
- iron
- lead
- magnesium
- mercury
- nickel
- sulfate

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium carbonate 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*. Sodium residue derived from using sodium carbonate in water softening is 30–300 mg/L.

STATUS

Sodium carbonate 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B201-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Benefi eld LD and Morgan JM (1999) Chemical Precipitation. In: *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed), American Water Works Association, 5th edition. McGraw-Hill Professional, 10.1–10.60.

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater,* 20th edition. American Public Health Association, Washington, DC.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

KIWA (1994) *Guideline quality of materials and chemicals for drinking water supplies*. Inspectorate of Public Health and Environmental Planning, Publication 94-01. Rijswijk, The Netherlands.

Lewis RJ (1993). *Hawley's Condensed Chemical Dictionary,* 12th edition. Van Nostrand Reinhold, New York.

NRC (National Research Council) (1982). *Water Chemicals Codex*. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

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

Sodium fluoride

(endorsed 2005)

Sodium fluoride is used to artificially fluoridate water, to reduce the occurrence of dental caries. Use of sodium fluoride is more common in small fluoridation facilities.

GENERAL DESCRIPTION

Sodium fluoride, NaF, is a white, odourless powder (or crystals), supplied in 25 kg bags. It is easily soluble in water, and the solubility varies little with temperature. It has a specific gravity of 2.78 at 20°C. The typical commercial grade of sodium fluoride is 97% purity, with about 44% fluorine. It has a bulk density of 1040–1440 kg/m^3. The pH of a 1% solution is 6.5; that of a 4% solution is 7.6. Suitable materials for handling sodium fluoride include iron, steel, fibreglass-reinforced plastic and polyethylene.

CHEMISTRY

Sodium fluoride is produced by neutralising hydrofluoric acid with either sodium carbonate or sodium hydroxide.

The dissolution of sodium fluoride in water forms fluoride ions (F^-) and sodium ions (Na^+) as follows:

$$NaF \Leftrightarrow Na^+ + F^-$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Sodium fluoride is used to artificially fluoridate water, to reduce the occurrence of dental caries. In each State and Territory, except for South Australia, the fluoridation of drinking water is regulated by an Act of Parliament; New South Wales and Queensland also have regulations in force.

Sodium fluoride can be used in solution feed systems at a strength of 1–2%, or in a saturator system where water is passed through a bed of sodium fluoride crystals, thus producing a saturated solution. The water used for dissolving sodium fluoride should not have a hardness greater than 75 mg/L (as calcium carbonate, $CaCO_3$), because the presence of calcium and magnesium causes the formation of insoluble fluorides which may cause clogging problems.

When using sodium fluoride, it is good practice to add the chemical after drinking water has been treated, because fluoride ions may be adsorbed onto the surfaces of suspended matter in water.

The target levels of fluoride in fluoridated water in Australia vary between 0.7 and 1.0 mg/L. The lower concentrations apply in warmer climates, where more water is consumed.

For sodium fluoride of 97% strength (44% F^-), this range translates to a dose of sodium fluoride of 1.6–2.3 mg/L.

CONTAMINANTS

Sodium fluoride can contain traces of free acid or alkali, and also:

- arsenic
- lead
- silicate
- sulfate

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

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium fluoride 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.*

Fluoride forms precipitates with many metals and other elements, but is notably insoluble with calcium; thus, scaling can occur when concentrated lime solution and concentrated fluoride solution come into contact. Locations for adding concentrated lime and fluoride solutions should be separated, to avoid this situation.

STATUS

Sodium fluoride 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B701-99. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Department of Health, South Africa (2003). *Water fluoridation, A manual for water plant operators.*

NSW Health (1957). Code of Practice for the fluoridation of public water supplies. *NSW Fluoridation of Water Supplies Act 1957*, NSW Government Gazette No. 135.

Sodium fluorosilicate

(endorsed 2005)

Sodium fluorosilicate, Na_2SiF_6, is used to artificially fluoridate water, to reduce the occurrence of dental caries.

GENERAL DESCRIPTION

Sodium fluorosilicate (Na_2SiF_6, also known as sodium silicofluoride, sodium hexafluorosilicate and disodium hexafluorosilicate) is a white or yellowish white, odourless, crystalline powder with a specific gravity of 2.7. Sodium fluorosilicate has very low solubility in water. The chemical is usually supplied at 98.5% purity (59.5% F^-) in 25 kg bags. It has a bulk density of 880–1150 kg/m^3. Suitable handling material includes cast iron, rubber linings, steel and stainless steel, fibreglass-reinforced plastic, polyethylene and polyvinyl chloride.

CHEMISTRY

Sodium fluorosilicate is produced by neutralising hydrofluorosilicic acid with sodium carbonate or sodium hydroxide, and then evaporating the solution.

The dissolution of sodium fluorosilicate in water forms the fluoride ion (F^-), as follows:

$$Na_2SiF_6 \Leftrightarrow 2Na^+ + SiF_6^{2-}$$

$$SiF_6^{2-} \Leftrightarrow SiF_4 + 2F^-$$

$$SiF_4 + 2H_2O \Leftrightarrow SiO_2 + 4F^- + 4H^+$$

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

Sodium fluorosilicate is used to fluoridate drinking water, to reduce the occurrence of dental caries. In each State and Territory, except for South Australia, the fluoridation of drinking water is regulated by an Act of Parliament; New South Wales and Queensland also have regulations in force.

It is good practice to add sodium fluorosilicate after drinking water has been treated, because fluoride ions may be adsorbed onto the surfaces of suspended matter in water. In water that has been treated and disinfected, sodium fluorosilicate is usually added at a concentration of 0.2%. A good mixing system is required because sodium fluorosilicate has low solubility in water.

The targeted levels of fluoride in fluoridated water in Australia vary between 0.7 and 1.0 mg/L. The lower concentrations apply in warmer climates, where more water is consumed. For sodium fluorosilicate of 98.5% strength (59.5% F^-), this range translates to a dose of sodium fluorosilicate of 1.2–1.7 mg/L.

CONTAMINANTS

Sodium fluorosilicate may contain traces of free acid and moisture, and also:

- arsenic
- cadmium
- iron
- phosphorus

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

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium fluorosilicate 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.*

Fluoride forms precipitates with many metals and other elements, but is notably insoluble with calcium; thus, scaling can occur when concentrated lime solution and concentrated fluoride solution come into contact. Points for adding concentrated lime and fluoride solutions should be separated, to avoid this situation.

STATUS

Sodium fluorosilicate 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B702-99. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

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NSW Health (1957). Code of Practice for the fluoridation of public water supplies. *NSW Fluoridation of Water Supplies Act 1957*, NSW Government Gazette No. 135.

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

Sodium hexametaphosphate

(endorsed 2005)

Sodium hexametaphosphate can be used for control of corrosion, prevention of scale formation, and sequestration of unwanted precipitants.

GENERAL DESCRIPTION

Sodium hexametaphosphate, $Na(PO_3)_6$ (also known as SHMP, glassy phosphate or vitreous phosphate) is a white granular powder with a bulk density of 800–1500 kg/m^3. It is highly soluble in water.

Sodium hexametaphosphate can be stored in rubber-lined containers, or in plastics, fibreglass-reinforced plastic, or stainless steel (type 316).

CHEMISTRY

Sodium hexametaphosphate is produced by treating soda ash or caustic soda with phosphoric acid.

Polyphosphates keep metal ions in solution for a period of time, thus preventing deposition.

With time, sodium hexametaphosphate naturally reverts to orthophosphate, and thus loses its sequestering capability. This reversion can be accelerated by low pH, high temperature and the presence of oxides of certain materials (e.g. iron, calcium, copper and zinc). The reversion can occur in hot water systems or in reverse osmosis (RO) membranes, where it can cause fouling.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In water treatment plants, a thin layer of sodium hexametaphosphate formed on metal surfaces is used to control corrosion. The chemical is also used as a sequestering agent, to prevent unwanted precipitates or scales (e.g. iron, manganese, calcium or magnesium) from depositing.

Control of ferrous iron through sequestering is only effective up to concentrations of 3 mg/L ferrous iron. In water treatment, the amount of sodium hexametaphosphate should be controlled to ensure that concentrations do not exceed levels that would complex manganese or iron by more than 10%. Control of calcium carbonate ($CaCO_3$) scale rarely requires more than 1 mg/L of polyphosphate.

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 this product (JECFA):

- arsenic
- iron
- fluoride
- lead

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium hexametaphosphate 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*.

Sodium and orthophosphate residues are present in finished water. Sodium hexametaphosphate naturally reverts to orthophosphate over time. Residual orthophosphate encourages biological growth.

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

The use of sodium hexametaphosphate in the water supply adds to the phosphorous load at the sewage treatment plant. Its use should therefore be considered in consultation with the manager of the sewage treatment plant.

STATUS

Sodium hexametaphosphate 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B502-01. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Gosselin RE, Smith RP and Hodge HC (1984). *Clinical Toxicology of Commercial Products*, 5th edition. Williams and Wilkins, Baltimore, II-121.

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NRC (National Research Council) (1981). *Drinking Water & Health*, Volume 4. National Academy Press, Washington, DC.

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

Sodium hydroxide

(endorsed 2005)

Sodium hydroxide is a commonly used alkali suitable for pH adjustment, water softening and corrosion control. It requires only a simple dosing system but needs care in handling.

GENERAL DESCRIPTION

Sodium hydroxide, NaOH (also known as caustic soda), is a white, deliquescent solid. It absorbs water and carbon dioxide from the air. The chemical is supplied as flake or pearl solids, or liquid (usually 30% or 46–50%). It has a specific gravity of 1.33 (at 30%) and 1.48 (at 46%). Liquid solutions of sodium hydroxide can freeze in cold climates, depending on concentration. Climate considerations are relevant for any caustic soda concentrations above 30%, because such solutions can freeze at temperatures above 0°C.

Appropriate handling materials for sodium hydroxide include rubber linings and steel, stainless steel, polyvinyl chloride, polypropylene, fibreglass-reinforced plastic.

CHEMISTRY

Sodium hydroxide is commonly produced by the electrolytic dissociation of sodium chloride, with chlorine gas as a by-product.

For pH and alkalinity adjustment, caustic soda simply produces hydroxide ions in water:

$$NaOH \Leftrightarrow Na^+ + OH^-$$

The chemical reactions of sodium hydroxide–soda softening are as follows:

$$CO2 + 2NaOH \Leftrightarrow Na_2CO_3 + H_2O \qquad (1)$$

$$Ca(HCO_3)_2 + 2NaOH \Leftrightarrow CaCO_3 + Na_2CO_3 + 2H_2O \qquad (2)$$

$$Mg(HCO_3)_2 + 4NaOH \Leftrightarrow Mg(OH)_2 + 2Na_2CO_3 + 2H_2O \qquad (3)$$

$$MgSO_4 + 2NaOH \Leftrightarrow Mg(OH)_2 + Na_2SO_4 \qquad (4)$$

$$CaSO_4 + Na_2CO_3 \Leftrightarrow CaCO_3 + Na_2SO_4 \qquad (5)$$

Sodium carbonate produced from equation (1) precipitates calcium noncarbonate hardness, as shown in equation (5). Sodium hydroxide can be used in combination with lime, depending on the amount of calcium noncarbonate to be removed.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sodium hydroxide is often used instead of powdered alkalis such as lime or soda ash, because the systems for adding sodium hydroxide are less complicated and require less maintenance. The chemical can also be used in place of lime to soften water by removing carbonate and noncarbonate hardness. Sodium hydroxide can also partially or fully substitute for the soda ash requirement.

Sodium hydroxide is used to raise pH and to convert excess carbon dioxide to alkaline species. Typical concentrations used are 2–100 mg/L (as caustic soda), but higher concentrations may be required with waters of poor quality.

Sodium hydroxide imparts a change of 1.55 mg/L calcium carbonate ($CaCO_3$) alkalinity per mg/L as

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

NaOH. Control of pH is difficult when sodium hydroxide is added to poorly buffered water.

For concentrations up to about 30%, caustic soda freezes at below 0°C. At 40% concentration, caustic soda will freeze at 15°C, dropping back to around 5°C at 46%. Concentrations above 50% freeze at 12°C or higher. In cold climates it may be necessary to dilute caustic solutions or heat caustic storage and delivery facilities. Softened water should be used for dilution to minimise scaling.

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 this product (JECFA, KIWA 1994, NRC 1982):

- arsenic
- iron
- cadmium
- lead
- chloride
- mercury
- chromium
- nickel

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium hydroxide 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 amount of sodium added to water when sodium hydroxide is used to adjust pH is generally insignificant.

STATUS

Sodium hydroxide 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B501-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Benefi eld LD and Morgan JM (1999). Chemical Precipitation. In: *Water Quality and Treatment, A Handbook of Community Water Supplies*, Letterman RD (ed), American Water Works Association, 5th edition. McGraw-Hill Professional, New York, 10.1–10.60.

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NRC (National Research Council) (1982). Water Chemicals Codex. Committee on Water Treatment Chemicals, Food and Nutrition Board, Assembly of Life Sciences, NRC, Washington, DC.

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

Sodium hypochlorite

(endorsed 2005)

Sodium hypochlorite is used as a disinfectant and oxidant in the treatment of drinking water. It provides available chlorine in a liquid form, with less risk than storing and handling chlorine gas.

GENERAL DESCRIPTION

Sodium hypochlorite, NaOCl, or liquid bleach, is a strong oxidising agent that is usually stored and used in solution. It has a disagreeable, sweetish odour and a pale greenish colour. Sodium hypochlorite solution releases vapours that cause corrosion in the presence of moisture.

Sodium hypochlorite is usually supplied as 10–13% w/v available chlorine. More concentrated solutions are not practical because of the instability of sodium hypochlorite, which forms chlorate and chlorite (both of which are of potential concern to health) as solution strength increases. Other factors that affect the stability of sodium hypochlorite are temperature, period of storage, impurities and exposure to light. The oxidising capability of 1 L of sodium hypochlorite (12.5% strength) is equivalent to the oxidising capability of 125 g of chlorine gas. Sodium hypochlorite is generated by combining chlorine and sodium hydroxide.

Suitable materials for storing and handling sodium hypochlorite include ceramics, glass, fibreglass reinforced plastic, polyethylene and polyvinyl chloride, and rubber or plastic linings.

CHEMISTRY

Sodium hypochlorite is generated by combining chlorine and sodium hydroxide.

Sodium hypochlorite hydrolyses in water forming hypochlorous acid (HOCl), which partially dissociates to hypochlorite ion (OCl^-):

$$NaOCl \rightarrow Na^+ + 2OCl^-$$

$$OCl^- + H_2O \Leftrightarrow HOCl + OH^-$$

The relative distribution of hypochlorous acid and hypochlorite ion resulting from these reactions depends on pH and temperature. 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 the 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.

Sodium hypochlorite is a base, which will raise the pH of water, whereas chlorine gas produces an acidic reaction that lowers the pH of the solution. The extent of the pH change will depend on the alkalinity of the water.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sodium hypochlorite is used as a disinfectant. Sodium hypochlorite solution is more expensive than chlorine, but its use is becoming more widespread, because of concerns about the safe transport and handling of hazardous gaseous chlorine in pressurised tanks.

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

Sodium hypochlorite 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).

Concentrations can range from 1 to 5 mg/L (as available chlorine), 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* (concentration × contact time) and chlorine residual; the World Health Organization (WHO) recommends 0.5 mg/L for 30 minutes. A free chlorine residual of more than 0.2 mg/L throughout the distribution system is preferred. In some systems, rechlorination is employed within the distribution system, with chlorine added after water has left the treatment plant, to boost chlorine residuals.

Superchlorination (10–50 mg/L as available chlorine) may be used to disinfect or clean tanks or pipelines. It can also be used to temporarily treat taste and odour issues caused by high ammonia levels. The 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 necessary when dealing with water containing ammonia.

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 sodium hypochlorite:

- chlorate
- iron
- manganese
- mercury
- nickel

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium hypochlorite 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. By-products include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, chloral hydrate and chloropicrine. Although many specific chlorine disinfection by-products have been identified, a significant percentage of the total organic halogens have yet to be identified.

Many factors affect the distribution of disinfection by-product species, including pH, temperature and levels of total organic carbon (TOC), bromide and chlorine. The THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform) are the best known chlorination by-products. Chlorinated THM, HAA and HAN species are generally present in higher concentrations than brominated species; however, brominated species predominate in high-bromide waters.

STATUS

Sodium hypochlorite 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.

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

REFERENCES

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B300-99. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

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White GC (1992). *Handbook of chlorination and alternative disinfectants*, 3rd edition. Van Nostrand Reinhold, New York.

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

Sodium silicate

(endorsed 2005)

Sodium silicate, in the form of 'activated silica,' is used as a coagulant or a flocculation aid in the treatment of drinking water, in conjunction with a primary coagulant (e.g. alum). Soluble silicates (waterglass) can also be used to inhibit corrosion or sequester metals, and sodium silicate solution can be used to adjust pH in small water systems.

GENERAL DESCRIPTION

Sodium silicate, $Na_2O{\cdot}xSiO_2$, can be in the form of lumps of greenish glass (soluble in steam), white powders of varying degrees of solubility, or as cloudy or clear solutions of varying viscosity.

Soluble silicates can be differentiated by their ratio of silica to sodium oxide (SiO_2:Na_2O). This ratio, which ranges from 1.6 to 3.3 by weight, determines the physical and chemical properties of the product. Liquid silicates with a ratio of 1.6 have a pH of 13.2; whereas, at a ratio of 3.3 the pH is 11.0. The specific gravity of these solutions ranges between 1.4 and 1.6. The colloidal and polymeric properties of liquid silicates increase as the SiO_2:Na_2O ratio increases.

Appropriate materials for handling sodium silicate include cast iron, steel, fibreglass-reinforced plastic and polyethylene, and rubber linings.

CHEMISTRY

Sodium silicate is produced by fusing high purity silica sand with sodium carbonate or potassium carbonate at 1000–1500°C. This results in an amorphous glass, which can be dissolved in water to form silicate solutions or 'waterglass'.

In solution, silica is present in equilibrium between monomeric anionic species. The proportion of silica and alkali in a sodium silicate is usually expressed as the weight ratio of SiO_2 to Na_2O.

In drinking water treatment, solutions of activated or colloidal silica can be used for coagulation. Such solutions can be generated on site by partial or complete neutralisation of a dilute solution of sodium silicate by a mineral acid, an acid salt or chlorine. The activated silica solution obtained can be slightly alkaline or neutral, and is aged for a short time (1–2 hours) before use. The solution is then further diluted with 2–2.5 volumes of water. The activated silica solution has a shelf life of 1–2 days.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

At one time, activated silica was commonly used as a coagulant aid (after a primary coagulant such as alum or ferric chloride), because it forms heavy, tough flocs that settle fast. However, polyacrylamide polymers have now largely replaced activated silica in most water treatment plants.

Soluble silicates are also used to protect metals from the corrosive effects of water by depositing a thin molecular film of silica (SiO_2) on metal surfaces. Silicate treatment is effective for corrosion control of concrete and a variety of metals: lead, copper, cast iron, ferrous metals, steel, galvanised steel, bronze, red and yellow brass, and nickel alloys. The pH and alkalinity of the water determine which silicate is suitable for this application.

Sodium silicate can also be used to sequester iron and manganese. Following metal oxidation, sodium silicate is added to hold oxidised metals in a colloidal suspension.

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

Concentrations of activated silica used in drinking water treatment can range from 1 to10 mg/L (as SiO_2), and the concentration required varies with water quality, depending on factors such as pH, turbidity, colour, temperature and contaminant level.

The effectiveness of sodium silicate as a corrosion inhibitor depends on water quantities such as pH and bicarbonate concentration. The chemical is more effective under high-velocity flow conditions. Silicate is effective at high pH, and at a dosage over 15–20 mg/L (as SiO_2).

Silicate with a high ratio of Na_2O to SiO_2 will raise pH in weakly buffered waters. For corrosion control, relatively high concentrations (up to 24 mg/L) are required during the first 30–60 days of treatment, to form the initial protective coating. Thereafter, the silicate dosage is reduced incrementally in 30-day periods, until it reaches maintenance doses (4–8 mg/L).

As a metal sequestrant, sodium silicate (as SiO_2) should be added at up to 4–5 times the level of iron or manganese in the water.

CONTAMINANTS

The purity of chemicals used in Australia for the treatment of drinking water varies, depending on the manufacturing process. More than 20 elements are present as trace impurities in sodium silicate, including:

- aluminium
- cadmium
- calcium
- chloride
- iron
- magnesium
- manganese
- sulfate

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

Sodium and silicate residues are present in finished water. When employed in drinking water treatment, sodium silicate 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*.

STATUS

Sodium silicate 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

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B404-98. AWWA CD-ROM (April 2003). Available at <www.awwa.org>

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Sodium tripolyphosphate

(endorsed 2005)

Sodium tripolyphosphate is used in drinking water treatment to control corrosion and soften water; it is also used as a sequestering and descaling agent, and to stabilise or disperse calcium and iron in the water distribution system.

GENERAL DESCRIPTION

Sodium tripolyphosphate, $Na_5P_3O_{10}$, is a white powder or granular solid, and is odourless. A 1% aqueous solution of sodium tripolyphosphate has a pH of 9.8; the pH of a concentrated solution (slurry) is about 10.5.

Appropriate handling materials for sodium tripolyphosphate include cast iron, steel, fibreglass-reinforced plastic, polyethylene and polyvinyl chloride; rubber-lined containers can also be used.

CHEMISTRY

Sodium tripolyphosphate is manufactured by combining soda ash or caustic soda with phosphoric acid. The product is then heated to form crystalline solids.

Low concentrations of polyphosphate inhibit the precipitation of calcium salts, and therefore inhibit scale formation. If phosphate concentrations are increased, then calcium phosphate precipitates. A further increase in concentration results in the sequestration phenomenon, whereby calcium is sequestered, inhibiting scale formation. Sequestering is affected by pH, with a neutral to alkaline pH being more effective.

Sodium tripolyphosphate can be used as a corrosion inhibitor in combination with divalent cations such as calcium (Ca^{2+}). Positively charged colloidal complexes form, migrate to the cathode and create an amorphous polymeric film. This inhibition is most effective at a pH of 6.5–7.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

The chemical is used in drinking water treatment to control corrosion and soften water; it is also used as a sequestering and descaling agent, and to stabilise or disperse calcium and iron in the water distribution system.

Polyphosphates can change the characteristics of corrosion, making it more uniform rather than a pitting type of corrosion. Polyphosphates have also been used to control oxidation of ferrous iron dissolved from pipes, and to reduce the formation of 'red water' (caused by contamination with hydrated iron oxide). When mixed with orthophosphate, polyphosphates may assist in the formation of an orthophosphate film, by complexing calcium or manganese in hard waters that might otherwise cause unwanted orthophosphate precipitates.

Typical doses for protection against scale, corrosion and prevention of 'red water' range from 0.5 to 20 mg/L, although doses of up to 50 mg/L may be used during mains cleaning.

For corrosion control in a cast-iron distribution system, an initial feed of 5–10 mg/L may be applied for several weeks, followed by a maintenance dosage of 1–2 mg/L; or a continuous dosage of 1–5 mg/L may be used.

For sequestration applications, a ratio of 3.4–5 parts sodium tripolyphosphate per water hardness (as $CaCO_3$) is recommended by manufacturers.

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

Control of post-precipitation in softened water typically requires a dosage of 0.5–2 mg/L.

Laboratory or pilot trials should be undertaken to determine the appropriate doses.

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 this product (JECFA):

- arsenic
- fluoride
- iron
- lead
- phosphates

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sodium tripolyphosphate 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*.

Sodium and orthophosphates are present in finished water and can cause problems. For example, phosphates increase biological activity in the distribution system, and polyphosphates both reduce the deposition of protective calcium-containing films and increase the solubility of metals, interfering with the formation of passivating films. Polyphosphates also soften asbestos-cement pipe by accelerating the depletion of calcium and inhibiting the formation of fibre-binding iron or manganese deposits. Similar effects can occur in cement-lined or concrete pipes.

The use of sodium tripolyphosphate in the water supply adds to the phosphorous load at the sewage treatment plant. Its use should therefore be considered in consultation with the manager of the plant.

STATUS

Sodium tripolyphosphate was endorsed by the NHMRC for use as a drinking water treatment chemical in 2005.

REFERENCES

ANSI (American National Standards Institute)/AWWA (American Water and Wastewater Association) Standard no B503-01. AWWA CD-ROM (April 2003). Available at www.awwa.org

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

JECFA (Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Joint Expert Committee on Food Additives). *Compendium of Food Additive Specifications*. FAO Food and Nutrition Papers 52 (two volumes). Available at https://www.who.int/foodsafety/publications/jecfa/en/

Lewis RJ (1993). *Hawley's Condensed Chemical Dictionary*, 12th edition. Van Nostrand Reinhold, New York.

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

Sulfuric acid

(endorsed 2005)

Sulfuric acid is used to correct pH in coagulation, water softening, corrosion control, prevention of post-precipitation and activation of silica.

GENERAL DESCRIPTION

Sulfuric acid (H_2SO_4) is a strongly corrosive, dense, oily liquid. It is colourless to dark brown, depending on purity, and is miscible with water. Sulfuric acid is generally available in concentrations of 28.5–98.5%, with corresponding specific gravity of 1.2–1.85 at 20°C. The acid is very reactive and dissolves most metals; the concentrated acid oxidises, dehydrates or sulfonates most organic compounds, often causing charring.

Sulfuric acid is highly corrosive to most metals and alloys, and is corrosive to mild steel at concentrations below 90%. It can be stored in fibreglass-reinforced plastic with acid resistant resins, polyethylene, porcelain, glass and rubber linings.

CHEMISTRY

Sulfuric acid is usually produced using the Contact process: sulfur dioxide is catalytically converted to sulfur trioxide, which is then dissolved in sulfuric acid and water.

Sulfuric acid disassociates in water to produce a strong acid:

$$H_2SO_4 \Leftrightarrow 2H^+ + SO_4^{2-}$$

Sulfuric acid is added to lime–soda softened waters to prevent post-precipitation of calcium carbonate and magnesium hydroxides in filters or in water distribution systems. These water usually have pH values of approximately 10.4, and are supersaturated with calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). Sulfuric acid is therefore used to reduce excessive pH values and alkalinities as follows:

$$H_2SO_4 + 2CaCO_3(s) \Leftrightarrow Ca\ (HCO_3)_2 + CaSO_4$$

$$H_2SO_4 + Ca(OH)_2 \Leftrightarrow CaSO_4 + 2H_2O$$

Sulfuric acid is used to fortify hydrolysing metal salts (aluminium and iron). The typical acid-fortified alum product, also called acidulated alum or acid alum, contains 5–20% (weight basis) of sulfuric acid. For a given amount of metal ion added to the water, strong acid-fortified products react with more alkalinity and depress the pH to a greater extent than nonfortified metal salt solutions.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, sulfuric acid is used to correct pH in coagulation, water softening, corrosion control, prevention of post-precipitation and activation of silica.

Handling and adding concentrated sulfuric acid to water requires extreme caution, because it can cause severe burns and eye damage. Also, sulfuric acid has an exothermic reaction with water that may cause violent splattering. Careful design is required in dilution systems for sulfuric acid, because the significant heating that may occur could damage pipework.

Concentrations of sulfuric acid required vary widely, depending on the alkalinity of the water and the pH required. Low concentrations (1–30 mg/L) are usually adequate to adjust pH for coagulation; higher doses may be required for water softening.

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

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 this product (JECFA):

- antimony
- arsenic
- cadmium
- chloride
- chromium
- copper
- fluoride
- iron
- lead
- manganese
- mercury
- selenium
- sulfate
- sulfur dioxide
- zinc

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, sulfuric acid 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*.

STATUS

Sulfuric acid 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

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Waterand Wastewater*, 20th edition. American Public Health Association, Washington, DC.

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Lewis RJ (1993). *Hawley's Condensed Chemical Dictionary*, 12th edition. Van Nostrand Reinhold, New York.

Schock MR (1999). Internal Corrosion and Deposition Control. In: *A Handbook of Community Water Supplies*, Letterman RD (ed), American Water Works Association, 5th edition. McGraw-Hill Professional, 17.1–17,109.

Zinc orthophosphate

(endorsed 2005)

Zinc orthophosphate is used to inhibit corrosion of lead, copper and iron, and to prevent the release of asbestos or cement from water pipes.

GENERAL DESCRIPTION

Zinc orthophosphate, $Zn_3(PO_4)_2$, solution is a clear odourless liquid that is soluble in water; it is available in various ratios of phosphate to zinc.

Appropriate materials for handling zinc orthophosphate include cast iron, steel, fibreglass-reinforced plastic, polyethylene and polyvinyl chloride; rubber-lined containers can also be used.

CHEMISTRY

Zinc orthophosphate is manufactured using zinc salts (chloride or sulfate) and orthophosphate. Zinc orthophosphate limits the release of lead, copper and iron from metal surfaces by forming a microscopic protective film on these surfaces, and by electrochemical passivation. Water with a high pH (> 8.1) should not be treated with zinc orthophosphate because of zinc hydroxide precipitation.

Reactions between orthophosphate and lead in water result in the formation of several solids that are less soluble than basic lead carbonate over a wide range of pH values. The most likely solid phase formed is hydroxypyromorphite ($Pb_5(PO_4)_3OH$). Tertiary lead orthophosphate ($Pb_3(PO_4)_2$) is another solid formed. The formation of lead orthophosphate films depends on the concentration of dissolved inorganic carbon (DIC; e.g. carbonates), acidity, temperature and orthophosphate content. These phosphate films may not form as rapidly as the basic lead carbonate solids. Carbonate competes with orthophosphate for control of lead solubility. Hence, lead orthophosphate films can be formed in water with low levels of carbonate or DIC (these two characteristics are often found together), in which case the effectiveness of a phosphate control program may need to be evaluated over a longer time.

TYPICAL USE IN AUSTRALIAN DRINKING WATER TREATMENT

In drinking water treatment, zinc orthophosphate is used to inhibit corrosion. It is particularly effective at inhibiting lead corrosion, because it reduces lead solubility in waters with both low and high alkalinity. The chemical is used to treat waters that are soft and corrosive. Zinc orthophosphate suppresses corrosion of carbon steel, and the release of asbestos fibres from asbestos–cement (A–C) pipe. It also inhibits corrosion of cast iron, and mildly inhibits corrosion of copper.

A few milligrams per litre of orthophosphate are sufficient at pH values in the 7–9 range.

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 this product:

- chloride
- sulfate

RESIDUAL AND BY-PRODUCT FORMATION IN DRINKING WATER

When employed in drinking water treatment, zinc orthophosphate 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*.

STATUS

Zinc orthophosphate was endorsed by the NHMRC for use as a drinking water treatment chemical in 1987. The revision undertaken in 2003 did not change the status of this chemical for the treatment of drinking water.

REFERENCES

Clesceri LS, Greenberg AE and Eaton AD (eds) (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.

Gosselin RE, Smith RP, Hodge HC (1984). *Clinical Toxicology of Commercial Products*, 5th edition. Williams and Wilkins, Baltimore, II-121.

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