

**Standard for the
Supply of Chlorine
for Use in Drinking-
Water Treatment**

First Edition

August 1997



STANDARD FOR THE SUPPLY OF CHLORINE FOR USE IN DRINKING WATER TREATMENT

First Edition

August 1997

The first edition of this standard was prepared for the Water Supply Managers' Group of the New Zealand Water & Wastes Association and the Ministry of Health by Opus International Consultants Ltd.

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FOREWORD

This Standard shall be used for supply and purchase of liquefied chlorine gas (commonly known as liquid chlorine), sodium hypochlorite, and calcium hypochlorite intended for drinking-water treatment.

When purchasing product under this Standard, the purchaser shall provide at least the following details.

1. Reference to this Standard.
2. Type of chlorine product required.
3. Quantity, form of shipment, and size of containers to be used.
4. Required delivery point and time.

Any modification of the provisions, definitions or terminology in this Standard must be provided in the purchaser's specifications.

1 GENERAL

1.1 Scope

This Standard covers the supply of liquefied chlorine gas (commonly known as liquid chlorine), sodium hypochlorite and calcium hypochlorite for use in the treatment of drinking-water. This Standard does not cover chlorine products for use in swimming pool water treatment.

1.2 Purpose

The main purpose of this Standard is to provide purchasers, manufacturers and suppliers with the minimum requirements for the above chemicals, including physical, chemical and testing requirements.

1.3 Application

This Standard can be referenced in specifications for purchasing and receiving liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite, and can be used as a standard for testing the physical and chemical properties of samples of such. The requirements of this Standard apply only when this document has been referenced and only to the above chemicals. It does not cover the use of chlorine dioxide or lithium hypochlorite.

1.4 Uses in Drinking-Water Treatment

Chlorine products are oxidising agents used for disinfection of water supplies. Chlorination can also reduce colour, tastes and odours in water and oxidise metallic substances to facilitate their removal during filtration - known as pre-chlorination¹. Liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite are the chlorine products commonly used in treatment of drinking-water supplies for this purpose.

1.5 Manufacture of Chlorine Products

- 1.5.1 In New Zealand chlorine gas for use in drinking-water treatment is manufactured at Kinleith in a membrane cell chlor-alkali plant (developed by Asahi Chemical Industry Co. of Japan). The process is an electrolytic one, but with a titanium anode separated from a steel cathode by a cation exchange membrane. The electrolyte used is very pure brine (solution of NaCl). Chlorine gas is produced at the anode, and sodium hydroxide produced at the cathode.

Chlorine gas is collected, dried, compressed and cooled to a point where it liquefies. Cylinders are filled so that liquid chlorine occupies about 90% of the cylinder when the temperature is about 60°C.

- 1.5.2 Sodium hypochlorite solutions for use in drinking-water treatment in New Zealand are either manufactured at Kinleith or in Christchurch by passing chlorine gas through a solution of caustic soda (known as the Lavel process).

On-site generation of sodium hypochlorite is achieved by using brine solutions and purpose built generating plants. The strength of sodium hypochlorite produced is about 0.8% free

¹ Because of concerns regarding the health effects and odours of some by-products produced during the pre-chlorination, it is a practice which should be avoided.

available chlorine (FAC) by weight. This Standard is not intended to cover on-site generation.

- 1.5.3 Calcium hypochlorite is generally produced by passing chlorine gas through a solution of calcium hydroxide (lime slurry). This produces calcium hypochlorite, calcium chloride and water. The calcium hypochlorite is dried by a special process with the inert calcium chloride substantially removed before packaging. All calcium hypochlorite used in New Zealand is imported.

1.6 Description of Chlorine Products

- 1.6.1 Liquefied chlorine gas (Cl_2) is a greenish-yellow gas/amber liquid with a pungent and irritating odour. As a greenish-yellow gas, the chlorine is present at a concentration many times greater than the level dangerous to humans. Chlorine gas at low concentrations is colourless, but may still be present at toxic concentrations. It is about 2.5 times as heavy as air so will seek the lowest level in an area of leakage.

Chlorine gas is acidic and oxidising. It is corrosive to metals and other substances, particularly when moisture is present.

Chlorine gas is a respiratory irritant. A tolerance to odour can be built up by regular exposure and therefore the sense of smell should not be relied upon to detect harmful levels. High concentrations (above 90 mg/m^3) in air cause coughing, laboured breathing and irritation of the eyes. At very high concentrations the difficulty in breathing may cause death by suffocation due to build up of liquid in the lungs. Liquefied chlorine causes skin and eye burns on contact.

- 1.6.2 Sodium hypochlorite (NaOCl) is generally a clear light-yellow aqueous solution, free from deposits or suspended matter, with a faint chlorinous odour. It is manufactured at between 14.8% and 16.5% (and can be up to 18%) free available chlorine by volume (ie, 14.8 to 16.5 kg FAC/100 L of product).

Light, heat, organic matter and certain heavy metal cations such as copper, nickel and cobalt accelerate the decomposition of sodium hypochlorite, with a resultant loss in chlorine strength. Decomposition produces an increase in chlorate ion (ClO_3^-) concentration. Good manufacturing techniques and proper storage of sodium hypochlorite will give a shelf life of at least 12 months, but the FAC content will decrease during this time.

Although not acidic, sodium hypochlorite solution is corrosive and will affect the skin and eyes on contact. Any affected areas should be washed with copious amounts of water. Personnel should wear gloves, apron, goggles and a suitable vapour mask when handling. Never add any other chemical to strong sodium hypochlorite solutions. Be extremely careful when adding chemicals to weakly chlorinated water - acids will produce chlorine gas (see Section 1.6.1), and ammonia compounds will produce highly irritating chloramines.

- 1.6.3 Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$ (approximately), is a white or yellowish-white granular powder, generally produced in granular or tablet form. It has a chlorinous odour and approximately 60 to 70% free available chlorine by weight (ie, 60 to 70 kg FAC/100 kg of product). When mixed to practical solubility levels ($30 \text{ g Ca}(\text{OCl})_2/\text{L}$ water) the expected level of FAC would be 1.8 to 2.1 kg FAC/100 L. The same factors for sodium hypochlorite decomposition apply. The presence of moisture appreciably decreases the life of metal containers due to its corrosive nature. Calcium hypochlorite has an expected shelf life in cool dry storage conditions of about 18 months to 2 years, but loses 2 to 3% FAC per year.

The same safety and handling precautions should be observed as for sodium hypochlorite above. Also, due to its oxidising properties, contact with flammable materials such as oil, grease, glycerine or printed matter should be avoided due to the highly reactive nature of such a combination.

1.7 Methods of Dosing

Chlorine gas is normally fed directly into water, via an injector and automatic shut down regulator, by means of a vacuum or positive pressure chlorinator. Pressure piping and connections should be minimised to decrease the possibility of leaks occurring.

Sodium hypochlorite is dosed from a corrosion resistant tank via a non-metallic pipe and corrosion resistant dosing pump, or by a polypropylene injector.

Calcium hypochlorite (in powder, granular or tablet form) must be dissolved in water and dosed as a settled, clear solution. When calcium hypochlorite is dissolved in water some insoluble sludge remains - this must not enter the feed line to the hypochlorinator. Solutions need to be prepared in advance, commonly by use of two tanks, to allow time for settlement. A float is attached to the feed line to ensure the solution is drawn from near the top of the tank and the last 100 mm cannot be drawn out.

1.8 Definitions

The following definitions shall apply in this Standard:

- | | | |
|-------|-------------------------------|--|
| 1.8.1 | <i>Calcium Hypochlorite</i> | Calcium hypochlorite $Ca(OC1)_2$ is a white or yellowish-white granular powder, granule or tablet with a chlorinous odour containing from 60 to 70% free available chlorine by weight. A saturated solution will have up to 12.6 kg FAC/100L of $Ca(OC1)_2$ solution at 25°C. It is often sold under a trade name. |
| 1.8.2 | <i>Sodium Hypochlorite</i> | Sodium hypochlorite solution $NaOC1$ is a clear light-yellow liquid with a faint chlorinous odour containing up to 18 kg/100 L free available chlorine. |
| 1.8.3 | <i>Liquefied Chlorine Gas</i> | Chlorine Cl_2 in its elemental state (commonly known as liquid chlorine), is normally packaged as a liquid under pressure in specially fabricated containers. |
| 1.8.4 | <i>Chlorine Products</i> | A group of chemicals or compounds, consisting of liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite, used for chlorination/disinfection of water. |
| 1.8.5 | <i>FAC</i> | Free available chlorine. |
| 1.8.6 | <i>Manufacturer</i> | The party that manufactures, fabricates, or produces materials or products. |
| 1.8.7 | <i>Purchaser</i> | The person, company or organisation that purchases any products or work to be performed. |
| 1.8.8 | <i>Reception Point</i> | The point of physical transfer of products from the supplier to the purchaser. |
| 1.8.9 | <i>Supplier</i> | The party who supplies product or services. A supplier may or may not be the manufacturer. |

2 MATERIALS

2.1 Physical Properties and Requirements

The following table shows some physical properties of some chlorine products.

| Property | Chlorine Product | | |
|----------------------|---|--|---|
| | Liquefied Chlorine Gas | Sodium Hypochlorite | Calcium Hypochlorite |
| Physical Description | An amber coloured liquid about 1.5 times more dense than water. At high concentrations in the gaseous state, it is a greenish-yellow gas about 2.5 times as dense as air. | A clear light yellow aqueous solution, free from deposits or suspended matter, with a faint chlorinous odour | A white or yellowish-white granular powder, granules or tablets with a chlorinous odour. |
| Molecular Formula | C12 | NaOC1 | Ca(OC1)2 (approx)*1 |
| Molecular Weight | 70.91 | 74.44 | 142.98 |
| Density | 1.408 kg/L @ 20°C *2 | 1.13-1.24 kg/L @ 20°C *3 | Bulk density: loose granular – 0.8 kg/L tablets – 1.9 kg/L Note: 1L = 1000 cm3 |
| pH | N/A (but acidic when dissolved in water) | 11 | N/A (but alkaline when dissolved in water) |
| Solubility in Water | 7 g/L at 20°C and 100 kPa | Completely miscible | 30 g/L *4 |
| Particle Size | N/A | N/A | Granular powder – not more than 10% passing a 100 (147µm) mesh screen. Tablets – uniform in shape and weight variance not more than 5% from average. Note more than 2% broken. |

Table 1: Some Physical Properties of the Different Forms of Aluminium Sulphate

- *1 Ca(OC1)2 is unstable and it is not possible to produce it in a pure form
- *2 at standard temperature and pressure
- *3 density varies with both FAC and excess NaOH content
- *4 30 g/L is practical solubility; theoretical is 180 g/L at 25°C.

2.2 Chemical Requirements

- 2.2.1 Liquefied chlorine gas shall be a minimum of 99.5% pure by volume as determined by the gas chromatographic test method (ASTM E 1746). Note that the Zinc Amalgam Method (ASTM E 412) may be used, but is now superseded by ASTM E 1746.
- 2.2.2 Sodium hypochlorite shall contain not less than 13.0 kg FAC/100l., of product (unless specified otherwise by the purchaser), on delivery at the reception point. All deliveries shall be clearly labelled to show the FAC content.
- 2.2.3 Calcium hypochlorite shall contain not less than 60 kg FAC/100 kg of product (unless specified otherwise by the purchaser), on delivery at the reception point. All deliveries shall be clearly labelled to show the FAC content

2.3 Impurities

2.3.1 General Impurities

In addition to any specific impurity limits, chlorine products shall not contain any other impurities that when dosed into water in accordance with accepted water treatment practice, may be deleterious to health or aesthetically objectionable as determined by the Drinking-Water Standards for New Zealand.

2.3.2 Liquefied Chlorine Gas

2.3.2.1 The moisture content shall not exceed 150 mg/kg. This is known as "dry chlorine".

2.3.2.2 The total non-volatile residue shall not exceed 150 mg/kg.

2.3.2.3 The sum of all heavy metals shall not exceed 30 mg/kg as lead equivalent. Individually, lead shall not exceed 10 mg Pb/kg, mercury shall not exceed 1 mg Hg/kg and arsenic shall not exceed 3 mg As/kg of liquefied chlorine gas.

2.3.2.4 Carbon tetrachloride shall not exceed 40 mg/kg.

2.3.2.5 Chloroform shall not exceed 300 mg/kg.

2.3.3 Sodium Hypochlorite

2.3.3.1 The total free alkali (expressed as NaOH) shall not exceed 18 g/L of solution and shall not be less than 3 g/L.

2.3.3.2 Insoluble matter shall not exceed 1.8 g/L of solution.

2.3.3.3 Some metals catalyse the decomposition of sodium hypochlorite solutions. The concentration of total iron shall not exceed 3 mg/L, and the concentration of each of cobalt, copper and nickel shall not exceed 0.05 mg/L of NaOCl solution.

2.3.4 Calcium Hypochlorite

Calcium hypochlorite granular powder or granules shall be free from lumps and not contain any dirt or other foreign material. In particular, sodium chloride content, a by-product of the manufacturing process, shall not exceed 180 g/kg.

2.3.5 Specific Impurity Limits

2.3.5.1 The limits of specific impurities in chlorine products (except those noted in Sections 2.3.2 to 2.3.4 inclusive) shall be as set out in Appendix A (unless set otherwise by the purchaser) to ensure that the product supplied is suitable for drinking-water treatment. Specific impurity limits shall be based on a chlorine dosage of 5 mg/L (unless the purchaser doses at a higher rate), the maximum acceptable value (MAV) of the impurity (taken from the Drinking-Water Standards for New Zealand 1995), and a minimum safety factor of 10.

2.15.2 Specific impurity limits shall be given as weight of impurity by weight of chlorine product (mg impurity/kg chlorine product), except for sodium hypochlorite which shall be by volume (mg impurity/L sodium hypochlorite solution).

3 DELIVERY

3.1 Packaging and Shipping

- 3.1.1 Chlorine products are toxic and oxidising and should be handled with care. Suppliers of chlorine products must comply with the relevant regulations for classification, marking, packaging, labelling, documentation (Dangerous Goods Declaration), and transporting of product; including the *Toxic Substances Regulations 1983*², the *Dangerous Goods Regulations (Class 2 - Gases 1980, and Class 5 - Oxidising Substances 1985)*, and the New Zealand Standard NZS 5433: 1988 *Code of Practice for the Transportation of Hazardous Substances on Land*.
- 3.1.2 Liquefied chlorine gas may be shipped in 4.5 kg, 33 kg, 70 kg or 920 kg cylinders, Calcium hypochlorite may be shipped in steel drums of various sizes (typically 40 to 50 kg), or suitable plastic containers. Sodium hypochlorite may be shipped in various drum sizes (20 L to 1000 L), or by a suitable bulk tanker. All sodium hypochlorite deliveries shall have a weight certificate as required in Section 7.3.1.
- 3.1.3 Tanks for transporting sodium hypochlorite shall comply with all conditions as required under the Transport Act and the Toxic Substances Regulations, and shall not contain any substances that might affect the quality of the sodium hypochlorite in treating water supplies as specified by this Standard.
- 3.1.4 For all deliveries (unless otherwise agreed with the purchaser), the manufacturer or supplier shall provide a certificate of compliance with this Standard, including the FAC content in the product.
- 3.1.5 All cylinders, drums and containers shall be in a good, safe condition and free from defects. Fittings on cylinders of liquid chlorine gas shall be free from corrosion, leak-proof and in good operating order to reduce any problems in connection at the point of use.

3.2 Labelling

Each shipment of product (packaging³, containers and vehicles) shall comply with NZS 5433 *Code of Practice for the Transport of Hazardous Substances on Land*, and specifically must be clearly identifiable and be marked and accompanied by documentation giving the following information:-

Contents: (Proper Shipping Name)
UN Number:
Hazard Class:
Name of Supplier:
Net Weight (Volume for sodium hypochlorite):
Name of Manufacturer:
Date of Manufacture (or Date Reference Code⁴):
FAC Level:

² The Toxic Substances and Dangerous Goods Regulations eventually will be replaced by regulations made the Hazardous Substances and New Organisms (HSNO) Act 1996. The existing regulations have been carried over into the new legislation, and will continue in force until at least mid 1997, possibly longer.

³ Package labeling does not apply to bulk deliveries.

⁴ Date Reference Code shall ensure traceability of product to manufacturing date, and for a bulk delivery to any sample taken on delivery.

The label shall be marked clearly with the words "Complies with NZWWA Standard for the Supply of Chlorine for Use in Drinking-Water Treatment" to avoid any confusion or use in drinking-water treatment of chlorine products intended for other purposes.

3.3 Unloading and Storage

- 3.3.1 Bulk sodium hypochlorite shall be unloaded at the purchaser's premises using either a gravity discharge or a pump into an appropriate receiving vessel. The supplier shall provide an appropriate "camlock" or other type of coupling as agreed with the purchaser for connection to the storage tank inlets, if required.
- 3.3.2 Drums or containers of sodium hypochlorite or calcium hypochlorite shall be transported on pallets for unloading with a forklift or by hand. They shall be stored in a cool, dry, covered designated storage area. Solutions should not be kept near sunlight.
- 3.3.3 Containers damaged prior to delivery shall be the responsibility of the supplier, and containers damaged during unloading at the purchaser's premises shall be the responsibility of the agent undertaking the unloading. Removal of damaged goods shall be as set out in Section 7.4.2. Chlorine cylinders and drums shall be stored in a safe manner (see Section 4.1.3).

4 HEALTH, SAFETY AND ENVIRONMENTAL PROTECTION

4.1 Requirements

- 4.1.1 Suppliers of chlorine products must comply with the requirements listed in Legislation in the References Section and NZS 5433: 1988. All practicable steps must be taken to protect the purchaser and others and the environment from hazards rising from the transportation, delivery and supply of chlorine products. As such, a plan or method statement for Health and Safety and Environmental Protection shall be submitted by the supplier with their tender.
- 4.1.2 Within two weeks of award of a contract to supply product or prior to delivery, the supplier shall provide to the purchaser the following information:
- (a) An updated copy of the Material Safety Data Sheet as detailed in Guidelines for the Preparation of Material Safety Data Sheets in New Zealand, published by the Occupational Safety and Health Service of the Department of Labour, May 1995.
 - (b) Evidence that drivers have been trained adequately, and have adequate knowledge and experience in the handling and delivery of chlorine products, including an endorsement on their licence as required under the Transport Act.
 - (c) Suppliers shall be responsible for carrying out vehicle and driver audits as defined in the Responsible Care Managers' Handbook. A copy of the audit checklist shall be provided to the purchaser on request (see Appendix D for an example audit form).
- 4.1.3 A copy of the purchaser's Health and Safety and Environmental Protection Management (HSEPM) Plan shall be made available to the supplier of chlorine products. Any practices by the supplier which do not comply with the Health and Safety Management Plan may be grounds for the termination of a supply contract.
- 4.1.4 A supplier may refuse to enter into a supply contract with a purchaser if the supplier is not satisfied with on-site practices of the purchaser, or inadequacies in the purchaser's HSEPM Plan.

4.2 Protective Equipment and Training

The purchaser and the supplier will be responsible for providing their respective personnel or agents with any necessary training, safety and protective equipment and ensuring it is used as required. At least two trained personnel should be involved in the loading/unloading, moving, connecting and/or changing of cylinders of liquefied chlorine gas. On occasions when it is not practical for a trained person provided by the purchaser to be present (i.e. isolated location and/or outside normal working hours), only one trained person may perform unloading of liquefied chlorine gas cylinders, subject to there being a reception and storage facility for the cylinders which is separate from the chlorine dosing room.

4.3 Spills

The supplier, their agent or the authorised purchaser's representative responsible for unloading the chlorine products, shall immediately report any spills within the grounds of the property in which the reception point is located. This action shall be as specified in the Health and Safety and Environmental Protection Management (HSEPM) Plan.

Where practicable, emergency showers shall be provided at reception points to enable personnel to “douche” themselves in the event of spillage of sodium hypochlorite or other chlorine products.

5 SAMPLING AND TESTING

5.1 Frequency

5.1.1 Liquefied Chlorine Gas

5.1.1.1 For liquefied chlorine gas supplied from the Kinleith plant⁵ referred to in Section 1.5.1, the sampling and testing frequency shall be six monthly for the following:

- (i) purity (assay) - (in terms of Section 2.2.1),
- (ii) moisture⁶ (in terms of Section 2.3.2.1),
- (iii) residue on evaporation (in terms of Section 2.3.2.2);

and yearly for the following impurities in terms of the specific impurity limits listed in Appendix A for liquefied chlorine gas:

- (iv) arsenic,
- (v) carbon tetrachloride,
- (vi) chloroform.

5.1.1.2 For liquefied chlorine gas not supplied from the Kinleith plant, the sampling and testing frequency shall be in accordance with the principles established in Section 5.1.2, but in terms of the purity limit (Section 2.2.1) and the impurity limits (as listed in Section 2.3.2) and the specific impurity limits listed in Appendix A for liquefied chlorine gas.

5.1.2 Sodium Hypochlorite

5.1.2.1 For sodium hypochlorite manufacturing processes which are continuous, the sampling and testing frequency for both the assay (Section 2.2.2) and the impurities (as listed in Section 2.3.3) shall be one monthly, unless the manufacturing plant and process is ISO 9002 certified, in which case the frequency may be reduced to three monthly. Sampling and testing of the specific impurity limits listed in Appendix A for sodium hypochlorite shall be carried out at least yearly, and also whenever the process and/or raw materials are changed.

5.1.2.2 For batch manufacturing processes, the sampling and testing for both the assay (Section 2.2.2) and the impurities (as listed in Section 2.3.3) shall be carried out on every batch. Sampling and testing of the specific impurity limits listed in Appendix A for sodium hypochlorite shall be carried out at least yearly, and also whenever the process and/or raw materials are changed.

5.1.2.3 Alternatively to Sections 5.1.2.1 and 5.1.2.2, sampling and testing may be done on each bulk delivery in terms of both the assay (Section 2.2.2) and the impurities (as listed in Section 2.3.3), subject to sampling and testing of the specific impurity limits listed in Appendix A for sodium hypochlorite being carried out by the manufacturer at least yearly, and also whenever the process and/or raw materials are changed.

⁵ This specific requirement for the Kinleith plant reflects the process' continuous nature and certification to ISO9002, its high degree of process monitoring, and the nature of the actual process and raw materials used, which combined, present a negligible risk of process contamination.

⁶ Moisture testing will commence after 1 October 1997.

5.1.2.4 Sampling and testing of the metals in sodium hypochlorite referred to in Section 2.3.3.3 shall be carried out at least yearly, and also whenever the process and/or raw materials are changed.

5.1.3 Calcium Hypochlorite

5.1.3.1 Except for calcium hypochlorite manufactured and certified in accordance with Section 5.1.3.2, a minimum of 2% of the number of the packages in each shipment shall be sampled. No sample shall be taken from a broken package. Samples from individual packages shall be combined to form a gross sample of at least 1.0 kg or as agreed. Testing shall be carried out for both the assay (Section 2.2.3) and the impurity limits (as listed in Section 2.3.4). Testing for the specific impurity limits listed in Appendix A for calcium hypochlorite shall be carried out at least yearly, and also whenever the manufacturer and/or process and/or raw materials are changed.

5.1.3.2 Calcium hypochlorite manufactured:

- (i) by a process which is certified to ISO 9002, and
- (ii) for which sampling and testing has been carried out on every batch for both the assay (Section 2.2.3) and the impurities (as listed in Section 2.3.4), and
- (iii) for which sampling and testing of the specific impurity limits listed in Appendix A for calcium hypochlorite has been carried out at least yearly, and also whenever the process and/or raw materials are changed, and
- (iv) for which the certification links every package to a unique batch number, shall be exempt from the requirements of Section 5.1.3.1.

5.2 Sampling and Sample Preparation

The sampling procedure shall be as set out in Appendix B of this Standard, unless otherwise agreed by the purchaser and supplier prior to the award of a contract to supply product.

5.3 Testing

5.3.1 The product shall be sampled and tested at the manufacturer's or supplier's own cost in order to provide a Certificate of Compliance as required in Section 7.1. Records of sampling and testing of representative samples, process monitoring results, and any other relevant records shall be made available to the purchaser on request.

5.3.2 The purchaser may randomly take samples of the product and have these samples analysed for conformance with this Standard. The cost of the analysis shall be paid by the supplier if the product does not meet the requirements of this Standard, and shall be paid by the purchaser if the product does meet the requirements of this Standard. These samples shall be taken at the place of manufacture and/or at the delivery point, as may be agreed upon by the manufacturer or supplier and the purchaser.

5.3.3 When inspection and sampling are to be conducted at the point of manufacture, the manufacturer shall afford the inspector representing the purchaser all reasonable facilities for inspection and sampling of finished product, which shall be so conducted as not to interfere unnecessarily with the operation of the plant.

5.3.4 Analytical testing methods shall be as specified in this Standard in Section 5.4.

- 5.3.5 If the analysis of a sample taken at the place of manufacture shows the product does not comply with the requirements of this Standard, the purchaser may require that the manufacturer provide a certified analysis from a Telarc registered laboratory (or equivalent) for successive deliveries. The cost of analysis shall be met by the manufacturer.
- 5.3.6 If the analysis of a sample taken at the point of delivery shows the product does not comply with the requirements of this Standard, a notice of non-conformance shall be provided by the purchaser to the supplier in accordance with Section 7.4.1. The cost of analysis shall be met by the supplier.

5.4 Standard Tests

- 5.4.1 Refer to the following standards for the standard tests for chlorine products:

Liquefied Chlorine Gas

| | |
|-------------------------------------|--|
| Assay | ASTM E 1746 (supersedes ASTM E 412) |
| Moisture and residues | ASTM E 410 (or for moisture, a method which has been validated against ASTM E 410) |
| Arsenic | AWWA B301 & Food Chemicals Codex |
| Carbon tetrachloride and chloroform | ASTM E 806 or ICI in-house procedure ⁷ |
| Lead | AWWA B301 & Food Chemicals Codex |
| Mercury | AWWA B301 & ASTM E506 |
| Heavy metals | AWWA IB301 & Food Chemicals Codex |

Sodium Hypochlorite

| | |
|-------------------------|------------------------|
| Free available chlorine | AWWA B300 Section 4.3 |
| Insoluble matter | AWWA 13300 Section 4.5 |
| Free alkali | AWWA 8300 Section 4.4 |

Calcium Hypochlorite

| | |
|-------------------------|-------------------------------|
| Free available chlorine | AWWA B300 Section 4.2 |
| Sodium chloride | Draft BS EN 900 Section 5.2.2 |

- 5.4.2 Test methods for specific impurities which are not given in the above standards shall be those in the current edition of Standard Methods for the Examination of Water and Wastewater (19th Edition, 1995 at time of drafting of this Standard) after suitable sample preparation, or as agreed between the manufacturer/supplier and the purchaser.

⁷ Developed at ICI Monod Division, reported in ICI Company Report B46495.

6 SUPPLY CONTRACT

6.1 Contract

The purchaser may enter into a contract with a supplier for the supply of liquefied chlorine gas, sodium hypochlorite or calcium hypochlorite, in accordance with this Standard.

6.2 Acceptable Conditions

Acceptable conditions of supply are outlined in Appendix C of this Standard, or as agreed between the supplier and the purchaser.

7 QUALITY ASSURANCE

7.1 Certificate of Compliance

The manufacturer or supplier shall provide the purchaser with a Certificate of Compliance. The Certificate of Compliance shall state that the product supplied to fulfil the purchaser's order complies with the applicable requirements of this Standard.

7.2 Method of Manufacture

If the method of manufacture, source and/or quality of raw material used is changed during the period of the supply contract, then this shall be advised. Any additional sampling and testing that may be required shall be at the manufacturer's or supplier's cost.

7.3 Weight Certificate

Delivered bulk product (sodium hypochlorite) shall be weighed over a certified weighbridge and the docket showing net weight produced on delivery.

7.4 Rejection

7.4.1 Notice of Non-conformance

If the chlorine product delivered does not meet the requirements of this Standard, a notice of non-conformance shall be provided by the supplier to the purchaser; or if the testing has been carried out by the purchaser, by the purchaser to the supplier. This must be within ten working days after receipt of the shipment at the delivery point. The notice of non-conformance shall stand unless either party notifies the other within five working days after receipt of the notice, that a retest is desired. On receipt of the request for a retest, the supplier shall forward to the purchaser one of the sealed samples taken in accordance with Appendix B. If the results from the retest do not agree with those obtained previously, the other sealed sample shall be forwarded for analysis to a referee laboratory agreed to by both parties. The results of the referee analysis shall be accepted as final. The cost of the referee analysis shall be paid by the supplier if the product does not meet the requirements of this Standard, and shall be paid by the purchaser if the product does meet the requirements of this Standard.

7.4.2 Produce Removal

7.4.2.1 If the product does not meet the impurity limit requirements of this Standard, the supplier shall remove the product from the premises of the purchaser within seven days of being requested to do so by the purchaser or such longer period as may be agreed. Removal of product shall be at no cost to the purchaser.

7.4.2.2 If the product meets the impurity limits but not the chlorine content requirements of this Standard, a price adjustment may be agreed between the supplier and the purchaser. In the event that a price adjustment cannot be agreed, the supplier shall remove the product from the premises of the purchaser if required by and at no cost to the purchaser.

- 7.4.2.3 The product that shall be removed shall include the rejected product and any other material the rejected product may have contaminated, for example contents of a tank into which a bulk delivery has been unloaded, if required by the purchaser.
- 7.4.2.4 All product removed shall be concurrently replaced with product conforming to this Standard with an appropriate compliance certificate at no cost to the purchaser or such monetary adjustment made as may be mutually agreed.

7.5 Audit

- 7.5.1 The purchaser may wish to carry out an audit of the supplier for conditions of delivery, health, safety, environmental protection and compliance with this Standard.
- 7.5.2 An audit shall only be carried out with due notification and agreement of the supplier. Due to the toxic nature of chlorine products (and the oxidising of some of them) the purchaser may wish to audit their own operation also. A guide audit checklist has been included as Appendix E to this Standard.

Appendix A: Specific Impurity Limits

Commercially available liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite are not known to contribute significant quantities of contaminants that adversely affect the potability of drinking-water.

Specific Impurity Limits (SIL) may be calculated based on a maximum dosage (MD) of chlorine/litre of water, and the maximum acceptable value (MAV) of a determinand taken from the *Drinking-Water Standards for New Zealand*, 1995. The safety factor (SF) used in the calculation shall be a minimum of 10, which reflects the convention that no more than 10 percent of MAV should be contributed by a given impurity in a water treatment chemical (the "1/10th" rule).

Purchasers may specify more stringent SILs to reflect their individual requirements.

The SIL values were determined using the following equation:

$$\text{SIL(mg/kg)} = \frac{\text{MAV (mg/L)} \times 10^6 \text{ mg/kg}}{\text{MD (mg/L)} \times \text{SF}}$$

where

| | | |
|-----|---|--------------------------|
| SIL | = | Specific Impurity Limit |
| MAV | = | Maximum Acceptable Value |
| MD | = | Maximum Dosage |
| SF | = | Safety Factor |

Note that for sodium hypochlorite the SIL must be converted to mg/L of product by multiplying by the density (*d*) of NaOCl (take as 1.2 kg/L):

$$\text{SIL (mg/L)} = \text{SIL (mg/kg)} \times d \text{ (kg/L)}$$

An example calculation is as follows:

| | | | |
|-------------------------|-----|---|---------------------------|
| Antimony ⁸ : | MAV | = | 0.003 mg/L |
| | MD | = | 5 mg/L as Cl ₂ |
| | SF | = | 10 |

$$\begin{aligned} \text{SIL (Sb)} &= \frac{0.003 \times 10^6}{5 \times 10} \\ &= 60 \text{ mg/kg Cl}_2 \end{aligned}$$

⁸ Note that antimony is not a known impurity in liquefied chlorine gas, but is used in this Standard as an indicator of possible heavy metal contamination of the hypochlorites.

For 99.5% pure liquefied chlorine gas, this SIL equates as follows:

$$\text{SIL} = 60 \text{ mg/kg Cl}_2 \times 0.995 = 59.7$$

$$= 60 \text{ mg Sb/kg of liquefied chlorine gas.}$$

For a 13% NaOCl solution (13 kg Cl₂ per 100 L) this SIL equates as follows:

$$\text{SIL} = 60 \text{ mg/kg Cl}_2 \times 0.13 = 7.8 \text{ mg Sb/L sodium hypochlorite}$$

For a 65% Ca(OCl)₂ product (65 kg Cl₂ per 100 kg of product) this SIL equates as follows:

$$\text{SIL} = 60 \text{ mg/kg Cl}_2 \times 0.65 = 27 \text{ mg Sb/kg of calcium hypochlorite.}$$

The following table contains recommended SILs which shall be tested for on an intermittent basis as set out in Sections 5.1 and 5.3. The SILs are based on MAVs from the *Drinking-Water Standards for New Zealand 1995*, a maximum dose rate of 5 mg/L as Cl₂ and a safety factor of 10. Note that where a Section number is given for the SIL for liquefied chlorine gas, the more stringent requirements (based on AWWA B301-92) given in those Sections of this Standard prevail.

| Determinand | Specific Impurity Limits | | | |
|----------------------|--|--|--|--|
| | Chlorine as Cl ₂ (mg/kg) | 99.5% pure Liquefied Chlorine Gas (mg/kg) | 13% Sodium Hypochlorite Solution (mg/L) | 65% Calcium Hypochlorite (mg/kg) |
| antimony | 60 | * | 7.8 | 17.6 |
| arsenic | 200 | Sect. 2.3.2.3 | 26 | 130 |
| cadmium | 60 | * | 7.8 | 17.6 |
| carbon tetrachloride | 40 | 40 | ** | ** |
| chlorate | 6000 | * | #780 | ** |
| chloroform | 4000 | Sect. 2.3.2.5 | ** | ** |
| chromium | 1000 | * | 130 | 650 |
| lead | 200 | Sect. 2.3.2.3 | 26 | 130 |
| mercury | 40 | Sect. 2.3.2.3 | 5.2 | 26 |
| nickel | 400 | * | 52 | 260 |
| selenium | 200 | * | 26 | 130 |
| trihalomethanes | 9200 | *** | ** | ** |

Table 2: Specific impurity limits for chlorine products

* Not a known impurity in liquefied chlorine gas

** Not a known impurity

*** Covered by the test for chloroform

No MAV is given in the *Drinking-Water Standards for NZ 1995*, however the *Guidelines for Drinking-Water Quality Management for NZ* suggest using the provisional MAV for chlorite of 0.3 mg/L.

Appendix B: Sampling Procedure

B1 Sampling Method

B1.1 General

- B1.1.1 Sampling and preparation shall be conducted as expeditiously as possible in order to avoid undue exposure of the product to the air.
- B1.1.2 The sampling method must give a gross sample that is representative of the product, and which may be divided to provide representative samples for analysis. Samples for analysis shall be taken in triplicate. Samples shall be sealed in airtight, moisture-proof containers.
- B 1.1.3 One sample is for the immediate use of the manufacturer or supplier for testing. The other two samples shall be retained until it is known from the results of the laboratory examination that the product meets the requirements of this Standard. The second sample shall be delivered to the purchaser if requested within five days of notification of the test results of the first sample, or such longer time as may be agreed. The third sample is for the use of a referee laboratory if there is a controversy over the analyses.
- B 1.1.4 Each sample shall be labelled to identify it by such information as the product, the batch number, and date and time of sampling. If the testing is on a shipment, the label shall also include the name of the purchaser and package number. Each label shall be signed by the sampler.

B1.2 Liquefied Chlorine Gas

- B 1.2.1 Samples shall be taken in 4.5 kg cylinders as set out in the appropriate test method given in Section 5.4, and also the Chlorine Institute Pamphlet 77.

B1.3 Calcium Hypochlorite

- B1.3.1 For powdered or granule forms, the product shall be sampled using a sampling tube that measures at least 20 mm in diameter.
- B1.3.2 For tablet form, the tablets shall be selected at random from each container sampled.
- B1.3.3 The gross sample, of at least 1.0 kg, or as agreed, shall be mixed thoroughly and divided to provide three 0.3 kg samples. These samples shall be sealed in air tight, moisture-proof, plastic or glass containers for use as described in Section B1.1.3.

B 1.4 Sodium Hypochlorite

- B1.4.1 A composite sample should be taken from the manufacturing process, or from the delivery tanker taken at five equally spaced time intervals during the unloading of the tanker. The total sample volume shall equal at least 1 litre or as agreed, and be collected in a clean glass or plastic container.
- B1.4.2 The gross sample (1 litre or as agreed) should be thoroughly mixed, and three 0.3 litre samples retained. They shall be sealed in air tight, moisture-proof plastic or glass containers for use as described in Section B1.1.3.

B2 Sample Preparation

- B2.1 Upon receipt of samples, appropriate preparation is important for accurate results, as poor preparation may lead to different test results from identical samples.
- B2.2 Sample handling and test procedures for sodium and calcium hypochlorites are detailed in AWWA Standard for Hypochlorites, ANSI/AWWA B300-92. Details for liquefied chlorine gas are given in the standard test methods outlined in Section 5.4.1 and the Chlorine Institute Pamphlet 77.

Appendix C: Supply Contract

C1 Contract

The following provides an outline of acceptable conditions of supply of product, to be included in a contract between a purchaser and a supplier for the supply of liquefied chlorine gas/calcium hypochlorite/sodium hypochlorite in accordance with this Standard, or as agreed by the purchaser and the supplier.

C2 Contract Period

A nominated contract period shall be set as part of a supply contract and shall commence from the date of entering into contract.

C3 Annual Requirements

An approximate annual requirement of product shall be provided for the information of the supplier. However, no guarantee can be given to these amounts as they will vary with water treatment plant throughput, water quality and customer consumption.

C4 Delivery

C4.1 The reception point for the supply of liquefied chlorine gas/calcium hypochlorite/sodium hypochlorite shall be designated and agreed between the supplier and the purchaser.

C4.2 Delivery of an order, to the purchaser's specified reception point shall be made within 7 days of receipt of the order or at any other mutually agreed time.

C4.3 Delivery of sodium hypochlorite shall be in full tanker or compartment loads, unless there is prior agreement between the supplier and the purchaser has been reached as to the load size.

C4.4 Delivery shall be made between the hours of 7.30 am and 4.00 pm Monday to Friday, excluding public holidays unless a prior arrangement is made between the supplier and the purchaser. The delivery shall be discharged only with the authorisation and in the presence of the purchaser's representative or operating personnel.

C4.5 Delivery dockets shall be provided giving the weight of the product and the proportion of free available chlorine. Bulk deliveries shall be weighed over certified weighbridges. Certificates of Compliance shall also be provided as agreed between the supplier and the purchaser.

C4.6 The purchaser may check the proportion of free available chlorine in the chlorine product after delivery.

C5 Payment

C5.1 Payment will be made in full by the purchaser by the 20th of the month following that in which deliveries are made and correctly invoiced by the supplier unless otherwise agreed.

C5.2 Invoices shall state the order number, docket number, weight of product supplied and the proportion of free available chlorine.

C5.3 Payment will be made on measured quantities unless otherwise agreed.

C6 Contract Sum

C6.1 Suppliers shall submit quotes in NZ\$/tonne or NZ\$/kg (NZ\$/litre for sodium hypochlorite) for the product offered. The quoted price shall allow for delivery including off-loading to the nominated reception points unless otherwise agreed.

C6.2 The quote shall hold firm for the duration of the contract period.

C6.3 The quote shall be exclusive of GST, but inclusive of any applicable duties or charges.

C7 Insurance

The supplier shall make their own arrangements for insurance of the order while in transit to the reception point. Responsibility will pass to the purchaser once the delivery has been made to the purchaser's storage facility.

C8 Subletting

The supplier shall not assign or sublet the contract or any part of the contract without the written consent of the purchaser.

C9 Cancellation

The purchaser shall reserve the right to cancel the contract for non-compliance with the Standard or failure to deliver within the allotted time.

Appendix D: Vehicle and Driver Audit

Carrier:

Driver's Name:

Vehicle Registration No:

Date of Audit:

The Driver

Yes

No

Is the Driver's licence endorsed "Hazardous Substances"?

Safety Equipment

Fire extinguisher with valid inspection date?

PVC rain suit?

Splash proof goggles?

Gloves?

Safety footwear?

Other appropriate equipment?

Is the above equipment compatible with the nature of the goods being carried?

Truck

Is the freight compartment in a clean condition?

Can the product be loaded and correctly segregated from other materials? (See Table 5 of NZS 5433 – for inter-island see IMDG code)

Yes **No**

Has the Driver the means to prevent load movement whilst in transit?

Has the vehicle a current certificate of fitness?

Documentation and Placarding

Are consignment notes for hazardous substances carried separate from all other documents?

Is the hazardous substances document holder marked appropriately?

Is the document holder located in the Driver’s door?

Has the vehicle got correct placarding for the products being transported? (See Table 3 of NZS 5433 or IMDG code if vehicle proceeding on sea transport)

Is the Driver aware of the correct procedures for the transport of hazardous substances?

If the answer to any of the above questions if “no”, the truck should not be loaded.

Inspected by: (Name)

..... (Signature)

..... (Position)

Appendix E: Audit Checklist

| Delivery of Product | Yes | No |
|--|--------------------------|--------------------------|
| Deliveries made on time? | <input type="checkbox"/> | <input type="checkbox"/> |
| Chlorine product clearly and adequately labelled? | <input type="checkbox"/> | <input type="checkbox"/> |
| Product delivered in specified containers? | <input type="checkbox"/> | <input type="checkbox"/> |
| Cylinders, drums and containers in good condition and defect free? | <input type="checkbox"/> | <input type="checkbox"/> |
| Correct equipment to enable safe practices during unloading? | <input type="checkbox"/> | <input type="checkbox"/> |
| Weigh certificate with bulk deliveries? | <input type="checkbox"/> | <input type="checkbox"/> |
| Chemical Requirements | | |
| Test/analysis results available? | <input type="checkbox"/> | <input type="checkbox"/> |
| Certificate of compliance with Standard? | <input type="checkbox"/> | <input type="checkbox"/> |
| FAC content in product as specified? | <input type="checkbox"/> | <input type="checkbox"/> |
| Any SILs exceeded? | <input type="checkbox"/> | <input type="checkbox"/> |
| Sampling/testing carried out in accordance with Standard? | <input type="checkbox"/> | <input type="checkbox"/> |
| Has method of manufacture changed since entering into contract? | <input type="checkbox"/> | <input type="checkbox"/> |

Health and Safety and Environmental Protection

Is safe practice applied in transport, delivery and off loading?

Is an updated MSDS supplied?

Proof of correctly trained drivers making deliveries?

Purchaser's Health and Safety and Environmental Protection Management Plan given to supplier?

Is safety equipment carried and used as instructed by plan?

Emergency plans in place for spill containment and clean-up procedures?

REFERENCES

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