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The New Zealand Water & Wastes Association Wai ora Aotearoa

WATER NEW ZEALAND
Good Practice Guide for the

SUPPLY OF ALUMINIUM SULPHATE FOR USE IN WATER TREATMENT

Third Edition - July 2016

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Contents

1 GENERAL

1.1 Scope

This Guide covers requirements for ensuring aluminium sulphate (commonly called alum) is of a suitable quality for use in drinking water treatment.

This Guide does not cover:

- environmental protection or health and safety measures associated with the chemical including, use, labelling, storage, transportation, packaging or disposal requirements, or
- operational procedures for using the chemical.

1.2 Purpose

The main purpose of this Guide is to provide purchasers, manufacturers and suppliers with the minimum physical, chemical and testing requirements for aluminium sulphate to meet safe limits for drinking water supplies. The requirements align with requirements for drinking-water safety outlined in the *Drinking Water Standards for New Zealand* (Ministry of Health, 2008).

1.3 Application

This Guide can be referenced in specifications for purchasing and receiving aluminium sulphate, and can be used as a guide for testing the physical and chemical properties of samples. The stipulations of this Guide apply when this document has been referenced and only to aluminium sulphate when used in water treatment.

The guide does not cover information requirements, packaging, equipment, transportation, disposal, safety or issues. Requirements for these aspects of water treatment chemical use are stipulated under New Zealand law and contained in the *Water Treatment Chemicals (Subsidiary Hazard) Group Standard 2006* (Environmental Protection Authority, 2006).

1.4 Legal Requirements

This Guideline is not intended to address supplier or operator legal responsibilities and should be considered alongside other requirements of New Zealand law. Legislation that relates to the supply and use of aluminium sulphate in drinking water supplies is:

- The Hazardous Substances and New Organisms (HSNO) Act 1996 (Ministry for the Environment, 2014)
- The Health (Drinking Water) Amendment Act 2007 (Ministry of Health, 2008)
- Land Transport Act 1998 (Ministry of Transport, 2012)
- Health and Safety at Work Act 2015 (Ministry of Business, Innovation, and Employment, 2015)
- Resource Management Act 1991 (Ministry for the Environment, 2015)

There may also be other legislation that needs to be complied with.

Legislated requirements for protecting the environment and the health and safety of people and communities from hazards associated with the use of aluminium sulphate are outlined in the HSNO Act. HSNO hazard classification and controls specific to aluminium sulphate can be found in the *Controls for Approved Hazardous Substances Database* available on the Environmental Protection Authority website: http://www.epa.govt.nz/

The use of aluminium sulphate for drinking water treatment is also covered by the *Water Treatment Chemicals (Subsidiary Hazard) Group Standard 2006* (Environmental Protection Authority, 2006). The Group Standard collates controls or conditions that apply to the use of aluminium sulphate in drinking water.

1.5 Uses in Water Treatment

Aluminium sulphate is used in water treatment for the coagulation of organic and mineral colloids prior to sedimentation and/or filtration. The alum destabilises fine colloidal suspensions and promotes the formation of conglomerations of this material bound in a chemical precipitate (called floc) which is able to be removed from the water by sedimentation, flotation and/or filtration.

1.6 Manufacture of Aluminium Sulphate

Aluminium sulphate is prepared from alumina bearing ores (aluminium trihydrate or bauxite) by treating with sulphuric acid at elevated temperatures. The supernatant solution is either decanted and sold in liquid form or concentrated and allowed to crystallise into a solid, dry, hydrated product.

1.7 Description of Chemicals

Aluminium sulphate is available in the following forms in New Zealand:

- Ground
- Lump (kibbled)
- Flaked
- Liquid

Ground alum is available in New Zealand as a fine white powder which comes in 25-50 kg bag lots.

Lump (kibbled) alum is in a lump form (approximately 10-75 mm sieve diameter size) and generally comes in 25-50 kg bag lots.

Flaked alum is in the form of flakes (approximately 1mm thick and varying from 3 – 25 mm across) and generally comes in 25-50 kg bag lots.

Liquid alum is usually a 47% weight for weight (w/w) solution that can either be purchased in 200 L drums or via bulk tanker.

1.8 Methods of Dosing

Aluminium sulphate is dosed as liquid solution, usually between 5-47% w/w. It is usually introduced via dosing pumps into an area of high water turbulence to facilitate rapid mixing of the alum with the recipient water. It is normal to pump the alum solution into additional dilution water when dosing strong solutions in order to facilitate good mixing and rapid coagulation in the raw water.

1.9 Definitions

The following definitions shall apply in this Guide:

1.9.1 *Alum:* Alum also refers to aluminium sulphate.

1.9.2 *Aluminium Sulphate:* The product of the reaction between sulphuric acid and aluminium trihydrate, with the general formula $Al_2(SO_4)_3.14H_2O$, but note that the number of waters of crystallisation is only approximate; commercial grades can vary from about 13.9-14.5H_20.

1.9.3 *cP* centipoise, a unit of viscosity (see Table 1).

1.9.4 *Delivery Point:* The point of physical transfer of materials from the supplier to the purchaser.

1.9.5 *Guideline Value:* Guideline values are the highest concentration of a determinand in the water that can be present without unduly impacting on the aesthetic properties of drinking water. Guideline values relate to determinands that do not pose a direct threat to public health, however may affect the appearance taste or smell of water. Guideline values are specified in the *Drinking Water Standards of New Zealand* (Ministry of Health, 2008).

1.9.6 *Manufacturer:* The party that manufactures fabricates or produces materials or products.

1.9.7 *Maximum Acceptable Value:* The highest concentration of a determinand in the water that, on the basis of present knowledge, is considered not to cause any significant risk to the health of the consumer over 70 years of consumption of that water. Maximum acceptable values are specified in the *Drinking Water Standards of New Zealand* (Ministry of Health, 2008).

1.9.8 *Purchaser:* The person, company or organisation that purchases any materials or work to be performed.

1.9.9 *Specific Impurity:* Substances which have a maximum acceptable value (MAV) or guideline value assigned to them in the *Drinking Water Standards of New Zealand* (Ministry of Health, 2008).

1.9.10 *Specific Impurity Limit:* Specific impurity limits are the maximum limit of an inorganic impurity given as weight of impurity by weight of product (mg of impurity/ kg of product) acceptable in a product.

1.9.11 *Supplier:* The party who supplies material or services. A supplier may or may not be the manufacturer.

1.9.12 *w/v:* Weight per volume.

1.9.13 *w/w:* Weight for weight.

2 MATERIALS

2.1 Physical Properties

Solid aluminium sulphate shall be dry, clean, and shall be lump, ground or flaked, as specified. Liquid aluminium sulphate is a nearly saturated solution of aluminium sulphate and shall be of such clarity as to permit the reading of storage tank contents with sight glasses without difficulty.

Some physical properties of the forms of alum are listed in Table 1.

Table 1: Some Physical Properties of Aluminium Sulphate

Property	Form of Aluminium Sulphate			
	Ground	Flaked	Kibbled	Liquid*
pH of 50% solution w/w	2.0	2.0	2.0	2.0-2.4
Specific Gravity	1.77	1.77	1.77	1.31-1.33 @ 15^{o}C
Bulk Density	1,100 kg/m^3	750 kg/m^3	800 kg/m^3	N/A
Particle Size	Min 90% < 6.3 mm sieve size, max 12% < 0.1 mm sieve.	3-25mm dia 1mm thick	10-75 mm sieve	N/A
Viscosity	N/A	N/A	N/A	27cP @ 10^{o}C 19 cP @ 20^{o}C

*Figures are given for a 47% w/w solution of aluminium sulphate.

2.2 Chemical Requirements

2.2.1 Lump (kibbled), ground, or flaked aluminium sulphate shall contain water-soluble aluminium of not less than 9.0% w/w as Al or 17.0% w/w as Al_2O_3.

2.2.2 Liquid aluminium sulphate shall contain water-soluble aluminium of not less than 4.23% w/w as Al or 8.0% w/w as Al_2O_3.

2.2.3 In lump, ground or flaked aluminium sulphate, the water-insoluble matter shall not exceed 0.5% w/w.

2.2.4 In liquid aluminium sulphate, the water-insoluble matter shall not exceed 0.2% w/w.

Note 1:

-the atomic weight of aluminium is 26.9815
-the atomic weight of oxygen is 15.9994
-so the molecular weight of Al_2O_3 is 101.9612
-so the conversion factor from Al to Al_2O_3 is 101.9612 ÷ 53.9630 = 1.889.

Note 2:

-the atomic weight of hydrogen is 1.0079
-the atomic weight of sulphur is 32.0600
-so the molecular weight of alum or $Al_2(SO_4)_3.14H_2O$ is 594.3486
-so the conversion factor from Al to "alum" is 11.014, or approximately 11.

Note 3:

-if an alum delivery has a specific gravity of 1.31 and it is 8.1% w/w Al_2O_3, then it is 4.288% w/w as Al, and 4.288 x 1.31 = 5.62% w/v Al, or 61.87% w/v as "alum".

2.3 Impurities

2.3.1 Specific Impurity Limits

2.3.1.1 For the purposes of this guide the term “specific impurities” refers to the following substances, which have maximum acceptable values (MAVs) or guideline values assigned to them in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008) and shown in Table 2.

2.3.1.2 The levels of specific impurities in commercially available aluminium sulphate shall not exceed the specific impurity limits (SILs) given in Table 2, which also specifies parameter values used for the calculation of the SILs. Calculations used to determine SILs are based on a maximum dose rate of 100mg/L and are shown in Appendix 1. MAV calculations have a safety factor of 10.

2.3.1.3 Specific impurity limits shall be given as weight of impurity by weight of product (mg of impurity/ kg of product).

2.3.1.4 SILs have been calculated for all inorganic impurities with MAVs in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008), but some of these are not included in Table 2 because the levels are unrealistically high. Consequently, SILs constituting more than 1% of the product have been deleted.

Table 2: Specific Impurity Limits for metallic and metalloid determinands, with MAVs and guidelines (GV) set in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008), and boron, fluoride and sulphide

Determinand	MAV or GV (mg/L)	mg of determinand per kg of	
		Solid product	Liquid product
		Minimum purity of product (w/w)	
		9% Al	*4.23% Al*
		99% $Al_2(SO_4)_3.14H_2O$	*46.6% $Al_2(SO_4)_3.14H_2O$*
Antimony	0.02	20	9
Arsenic	0.01	4	2
Barium	0.7	690	320
Boron	1.4	1300	650
Cadmium	0.004	3	1
Chromium	0.05	40	20
Copper*	1	900	460
Fluoride	1.5	1400	690
Lead	0.01	4	2
Manganese*	0.04	390	180
Mercury	0.007	6	3
Molybdenum	0.07	60	30
Nickel	0.08	70	30
Selenium	0.01	9	4
Sulphide*	0.05	490	230
Uranium	0.05	20	9
Zinc*	0.02		6900

* These determinands are either aesthetic determinands, having only a guideline value, or are health significant determinands, having both an MAV and a guideline value. In the latter case, the lower of the two is given in the table.

2.3.2 General Impurities

Additional impurity limits may be specified by the purchaser to ensure the material supplied is suitable for water treatment. If additional impurity limits are specified, the purchaser must specify the methods to be used to show that these limits have been met.

Additional impurity limits may be warranted in situations where impurities are impacting treatment plant operations or where determinands listed in Table 2 occur at elevated levels in source water.

3 TEST METHODS

3.1 General

3.1.1 The manufacturer or supplier shall test the materials at their own cost in order to provide a Certificate of Compliance as required in Section 4.1.

3.1.2 The purchaser may take samples of the material at random and have these samples analysed for conformance with this Guide, at the cost of the purchaser. 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.

3.1.3 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 material, which shall be so conducted as not to interfere unnecessarily with the operation of the plant. When on site, the purchaser must follow the manufacturing site's safety policies and procedures when taking the sample, or allow the manufacturer to take the sample itself while under supervision of the supplier's representative.

3.1.4 Analytical methods shall be as specified in this Guide in Section 3.4.

3.1.5 Laboratories undertaking analyses to show that a product complies with the requirements of this Guide shall be suitably accredited for the tests being undertaken. A New Zealand laboratory shall be IANZ accredited and overseas laboratories shall have ISO 17025 accreditation.

3.1.6 If the analysis of a sample taken at the point of delivery shows the material does not comply with the requirements of this Guide, a notice of non-conformance must be provided by the purchaser to the supplier in accordance with Section 4.3.1.

3.2 Sampling

3.2.1 The sampling procedure set out in Appendix B of this Guide shall be followed.

3.3 Standard Tests

3.3.1 The Standard *AWWA B403-09 Aluminum Sulfate – Liquid Ground Lump* (American Water Works Association, 2009) is to be referred to for standard tests for the following properties:

- Specific Gravity
- Water Insoluble Matter
- Total Soluble Alumina and Aluminium
- Total Water Soluble Iron
- Ferric Iron
- Ferrous Iron
- Basicity and/or Free Acid.

3.3.2 Test methods for specific impurities listed in Table 2, shall be determined by test methods found in *Standard Methods for the Examination of Water and*

Wastewater, *22nd Edition* (E.W. Rice, 2012). The purchaser must state which of the testing methods is to be used to determine compliance with the specific impurity limits.

3.4 Test Frequency

3.4.1 Base frequency of testing for impurities

The sampling and certified analysis on which the Certificate of Compliance of a product is based (section 4.1.3) must occur at least annually for all impurities listed in Table 2. Sampling and analysis must also be carried out:

i. whenever the process and/or raw materials changes, in which case all impurities in Table 2 must be tested, and
ii. at the frequency listed in Table 3 if any test shows the concentration of an impurity in the product exceeds 50% of its SIL, in which case only the impurities exceeding 50% of their SIL need be tested.

Table 3: Test frequency of product impurity limits (specified in section 2.3)

Property	Test Frequency
Fluoride	Per batch, or weekly if multiple batches are received in a week
Other determinands listed in Table 2	Per batch, or monthly if multiple batches are received in a month

3.4.2 Soluble aluminium and water insoluble matter

Tests for water soluble aluminium and water insoluble matter (outlined in 2.2) should be undertaken per batch.

3.4.3 P2a determinands

Compliance with the chemical requirements of the Drinking Water Standards for New Zealand (Ministry of Health, 2008) for P2a determinands can be demonstrated using the alternative approach given in section 8.2.1.2 of the Standards. This requires a certified analysis stating the concentration of the P2a determinand in the product as provided for in section 4.

4 QUALITY ASSURANCE

4.1 Certificate of Compliance

4.1.1 The manufacturer or supplier shall provide the purchaser with a certificate of compliance with each delivery that states that the material furnished in accordance with the purchaser's order complies with all applicable requirements of this Guide.

4.1.2 The purchaser shall not use a delivered product until a certificate of compliance for that delivery is received from the chemical supplier, and the supplier has demonstrated that there is a satisfactory system in place to ensure the quality of the product between the point of manufacture and point of delivery.

4.1.3 The chemical supplier shall provide a certified analysis of the material, from a mutually agreed upon IANZ or ISO 17025 accredited laboratory, showing that the requirements of Sections 2.3 and 3.3 have been met at test frequencies outlined in 3.4.

4.1.4 If the method of manufacture, source and/or quality of raw material used is changed during the contract period, additional samples shall be tested by the supplier to demonstrate that the changes have not affected conformance with this Guide. A copy of the certificate of compliance shall be provided to the purchaser.

4.2 Product Volume

The volume of bulk product delivered shall be determined by certified instrumentation, and record from the instrumentation of the volume delivered provided to the purchaser.

4.3 Rejection

4.3.1 **Notice of Non-conformance**

If the aluminium sulphate delivered does not meet the requirements of this guide or the additional impurity limits notified by the purchaser (Section 2.3), a notice of non-conformance must be provided by the purchaser to the supplier within 30 working days after receipt of the shipment at the point of destination. The results of the purchaser's tests shall prevail unless the supplier notifies the purchaser within five working days after receipt of the notice of complaint that a retest or inspection is desired. On receipt of the request for a retest, the purchaser shall forward to the supplier one of the sealed samples taken in accordance with Section 3. In the event that the results obtained by the supplier upon retesting do not agree with the results obtained by the purchaser, the other sealed sample shall be forwarded, unopened, for analysis to a referee laboratory agreed upon by both parties. The results of the referee analysis or inspection shall be accepted as final.

The cost of the referee analysis shall be paid by the supplier if the material does not meet the requirements of this guide and shall be paid by the purchaser if the material does meet the requirements of this guide.

4.3.2 **Material Removal**

4.3.2.1 If the material does not meet the impurity limit requirements of this Guide, the supplier shall remove the material from the premises of the purchaser when requested by the purchaser. Removal of material shall be at no cost to the purchaser.

4.3.2.2 If the material meets the impurity limits but not the water soluble aluminium content requirements of this Guide, a price adjustment may be agreed between the supplier and the purchaser. In the event that a price adjustment cannot be agreed upon, the supplier shall remove the material from the premises of the purchaser if required by, and at no cost to, the purchaser.

4.3.2.3 The material that shall be removed shall include the rejected material and any other material the rejected material may have contaminated, for example, contents of a tank into which a bulk delivery has been unloaded, if required by the purchaser.

4.3.2.4 All material removed shall be concurrently replaced with material conforming to this Guide with an appropriate compliance certificate at no cost to the purchaser.

Appendix A: Specific Impurity Limits

A 1 Calculations for Specific Impurity Limits

Calculations are based on a maximum dose of 100 mg of aluminium sulphate per litre of water. Health related SILs in Table 2 are calculated using the following equation:

$$SIL\ (mg/\ kg) = \frac{MAV\ (\ mg\ /\ litre\ )\ x\ 10^6\ (\ mg\ /\ kg)\ x\ P}{MD\ (\ mg\ /\ litre\ )\ x\ SF\ x\ 100}$$

Where SIL = Specific Impurity Limit

MAV = Maximum Acceptable Value of the impurity determinand set in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)*

MD = Maximum Dose of aluminium sulphate $(Al_2(SO_4)_3).14H_2O$

SF = Safety Factor

P = Purity - minimum percentage of aluminium sulphate in the product

The SILs are calculated based on:

1. The MAV or guideline value (GV) for each determinand taken from the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008).
2. A maximum dose (MD) of 100 mg aluminium sulphate $(Al_2(SO_4)_3)$/litre of water
3. A safety factor (SF) of 10, which reflects the view that no more than 10 percent of a MAV should be contributed by a given impurity in a water supply chemical. Arsenic and lead have been assigned a safety factor of 20, reflecting recent concerns amongst some public health practitioners of the impact on these impurities on public health.

Inclusion of a determinand in Table A.1 is not an indication that the products are expected to contain the impurity, or, if present, that the impurity will occur near its calculated SIL.

A3 Example Specific Impurity Limit Calculations

Example calculations are as follows:

Arsenic in solid alum:

MAV = 0.01 mg/L
MD = 100 mg/L
SF = 10
P = 99% $(Al_2(SO_4)_3).14H_2O$

$$SIL = \frac{0.01\ (\ mg\ /\ litre\ )\ x\ 10^6\ (\ mg\ /\ kg)\ x\ 99}{100\ (\ mg\ /\ litre\ )\ x\ 10\ x\ 100}$$

$$SIL = \frac{9.9\ mg}{kg} \quad of\ solid\ alum$$

Rounding down to one significant figure, yields

$$SIL = \frac{9\ mg}{kg} \quad of\ solid\ alum$$

Iron in liquid alum:

GV = 0.2 mg/L
MD = 100 mg/L
P = 46.6% $Al_2(SO_4)_3).14H_2O$)

$$SIL = \frac{0.2\ (mg/litre) \times 10^6\ (mg/kg) \times 46.6}{100\ (mg/litre) \times 100}$$

$$SIL = \frac{932\ mg}{kg} \quad of\ liquid\ alum$$

Rounding down to two significant figures, yields

$$SIL = \frac{930\ mg}{kg} \quad of\ liquid\ alum$$

Appendix B: Sampling Procedure

B 1 Sampling Method

B 1.1 General

B 1.1.1 Sampling and preparation shall be conducted as expeditiously as possible in order to avoid undue exposure of the material to the air, thus avoiding contamination and evaporation.

B 1.1.2 The sampling method must give a gross sample that is representative of the material, and which may be divided to provide representative samples for analysis. The quantity of sample required by the testing laboratory to carry out the desired tests must be known prior to the sample being taken.

B 1.1.3 Samples for analysis shall be provided in triplicate. One sample is for the immediate use of the purchaser for testing of the shipment. The other two samples shall be retained until it is known from the results of the laboratory examination that the shipment meets the requirements of this guide. The second sample shall be delivered to the supplier if requested within five days of notification of the examination results of the first sample. The third sample is for the use of a referee laboratory if there is a controversy over the analyses.

B 1.1.4 Samples shall be sealed in airtight, moisture-proof containers supplied by the analysing laboratory.

B 1.1.5 Each sample shall be labelled with the minimum information as follows: the material name, the name of the purchaser, the name of the sampler, package number, date sampled, and date received. Each label shall be signed by the sampler.

B 1.2 Risk Assessment and Management

B 1.2.1 Before collecting samples, the sampler shall assess the risks to their own safety, and to others in the vicinity, of taking the sample (e.g. the release of dust from powdered or crystalline material, splashing or spillage of liquid product), identify what measures can be taken to minimise these risks (e.g. different approach for taking the sample, dust masks, protective clothing), and take these steps.

B 1.2.2 Where possible, samples should be taken by an experienced laboratory technician.

B1.3 Sample Size

B1.3.1 The sample size must provide a gross sample that is representative of the material.

B1.3.2 The size of the gross sample and the samples for analysis shall be agreed upon by the purchaser and the supplier, giving consideration to obtaining representative samples and the requirements of the laboratory to undertake analyses.

B1.4 **Solid Aluminium Sulphate**

B1.4.1 If the alum is packaged, 5% of the number of the packages shall be sampled. No sample shall be taken from a broken package.

B1.4.2 Care shall be taken to include a proportional amount of lumps and fines, to obtain representative material.

B1.4.3 Ground aluminium sulphate shall be sampled using a sampling tube or other effective device that measures at least 2 cm in diameter.

B1.4.4 Kibbled alum (or lumps) shall be sampled from the container by removing an assortment of different sized lumps by hand (wearing clean gloves).

B1.4.5 The gross sample, of at least 16 kg or as agreed, shall be crushed if necessary and mixed thoroughly and divided to provide three 0.5 kg samples. These samples shall be sealed in air tight, moisture-proof, glass containers.

B1.4.6 Each sample container shall be labelled for identification and signed by the sampler.

B 1.4 **Liquid Aluminium Sulphate**

B1.4.1 For safety reasons, samples shall be taken from the tanker after it has been filled. A gross sample shall be taken, the total volume of which shall be no less than three times the volume required for Section B1.4.2.

B1.4.2 The gross sample shall be thoroughly mixed, and split into three subsamples as provided for in Section B1.1.3. The containers for the subsamples shall be supplied by the laboratory for the tests listed in Section 3.3. More than one container may be required for each subsample.

B 1.4.3 Each sample container shall be labelled for identification and signed by the sampler.

B2 Sample Preparation

B2.1 The preparation of subsamples for testing may affect the results obtained from identical samples so appropriate and consistent preparation procedures are most important.

B2.2 An appropriate preparation technique must be agreed upon by the purchaser and the supplier.

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A consistent approach across the 3 waters sector