

Australian Standard[®]

**Refractories and refractory materials—
Chemical analysis**

Part 4: Dolomites and magnesites



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 - Australasian Institute of Mining and Metallurgy
 - Bureau of Steel Manufacturers of Australia
 - CSIRO Manufacturing and Infrastructure Technology
 - Cement Industry Federation
 - Institute of Refractories Engineers
 - Refractories Manufacturers Association of Australia
 - The University of New South Wales
-

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Australian Standard[®]

Refractories and refractory materials— Chemical analysis

Part 4: Dolomites and magnesites

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PREFACE

This Standard was prepared by the Standards Australia Committee MN-007, Refractories and Refractory Materials, to supersede AS 2503.4—1987.

Other parts of the Standard describing the chemical analysis of other refractory materials are as follows:

Part 1: Silica refractories

Part 2: Aluminosilicate refractories

Part 3: High alumina materials

Part 5: Chrome-bearing materials

In preparing the original edition of this Standard, the Committee drew extensively upon the corresponding work of ISO/TC 33, Refractories, and the methods specified in BS 1902, *Methods of testing refractory materials*.

This Standard utilizes titrimetric, UV-Visible spectrophotometric and flame photometric methods of analysis and, like its companion parts, includes flow sheets depicting the scheme of analysis.

The objective of this revision is to bring the Standard into alignment with current Style.

The term ‘informative’ has been used in this Standard to define the application of the appendix to which it applies. An ‘informative’ appendix is only information and guidance.

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STANDARDS AUSTRALIA

Australian Standard

Refractories and refractory materials—Chemical analysis

Part 4: Dolomites and magnesites

SECTION 1 SCOPE AND GENERAL

1.1 SCOPE

This Standard sets out methods for the sampling, preparation of samples and analysis of dolomite and magnesite refractories and refractory materials. Procedures are described for determining—

- (a) the loss on ignition*;
- (b) the chemical composition*, i.e. the amount of silicon, iron, titanium, manganese, chromium, aluminium, magnesium, calcium, sodium, potassium and lithium present in magnesites and dolomites, expressed as the oxides of these elements; and
- (c) the boron content of magnesites expressed as boron (III) oxide.†

This Standard applies to dolomites and magnesites whose composition is typified by Table 1. It may be applicable to materials which fall outside these ranges subject to agreement between interested parties.

1.2 REFERENCED DOCUMENTS

The following Standards are referred to in this Standard:

AS	
2162	Verification and use of volumetric apparatus (series)
2497	Procedures for acceptance testing of refractory products
2497.1	Part 1: Batch procedure
2780	Refractories and refractory materials—Glossary of terms
3753	Recommended practice for the chemical analysis of materials by ultraviolet/visible spectrophotometry
AS/NZS	
2243	Safety in laboratories (series)

* The original paper on which the methods are based was written by Bennett, H. and Reed, R.A., *The ANALYST*, 96 (1971), pp 640-655.

† The method described is based on an article by Skelton, N.F.C. and Reed, R.A., *The ANALYST*, 101 (1976), pp 396-403.

TABLE 1
APPLICABILITY OF TEST METHODS AND TYPICAL COMPOSITION OF
DOLOMITES AND MAGNESITES

Elemental constituent	Expressed as	Concentration limit for test method (percent, <i>m/m</i>)	Typical composition (percent, <i>m/m</i>)	
			Magnesites	Dolomites
Magnesium	MgO	0.1	40 to 98	15 to 45
Calcium	CaO	0.05	≤ 5	25 to 60
Silicon	SiO ₂	0.02	≤ 5	≤ 5
Iron	Fe ₂ O ₃	0.2	≤ 5	≤ 5
Chromium	Cr ₂ O ₃	0.005	≤ 2	≤ 2
Aluminium	Al ₂ O ₃	0.05	≤ 2.5	≤ 2.5
Titanium	TiO ₂	0.02	≤ 0.5	≤ 0.5
Manganese	MnO	0.01	≤ 0.5	≤ 0.5
Sodium	Na ₂ O	0.05	≤ 0.5	≤ 0.5
Potassium	K ₂ O	0.05	≤ 0.5	≤ 0.5
Lithium	Li ₂ O	0.05	≤ 0.5	≤ 0.5
Boron	B ₂ O ₃	0.001	≤ 0.3	not applicable

NOTE: The values given in column 3 represent the lowest concentration of constituent for which the test methods described in this Standard are considered to produce accurate results.

1.3 DEFINITIONS

For the purpose of this Standard, the definitions given in AS 2780 and those below apply.

1.3.1 Dolomite refractory

A basic refractory consisting essentially of calcined or stabilized dolomite.

1.3.2 Magnesite refractory

A refractory consisting essentially of magnesite.

1.4 REPEATABILITY

Duplicate determinations should be carried out in all cases. It is recommended that the analyses be repeated if the difference between duplicate determinations for elemental constituents, expressed as in Column 2 of Table 1, exceeds the following limits:

- (a) For a constituent exceeding 30 percent, *m/m*..... 0.3 percent max.
- (b) For a constituent between 10 percent and 30 percent, *m/m* 0.2 percent max.
- (c) For a constituent between 5 percent and 10 percent, *m/m* 0.1 percent max.
- (d) For other constituents amounting to less than 5 percent, *m/m* 0.05 percent max.

NOTE: The difference referred to is the percentage difference between the actual values obtained for the component relative to the test sample NOT the percentage difference between the values relative to the constituent, e.g. if the magnesium content was determined from duplicates to be 44.1 percent and 44.3 percent then the difference referred to here is (44.3–44.1) percent not

$$\left(\frac{44.3 - 44.1}{44.1} \times 100 \right) \text{ percent}$$

1.5 PRINCIPLE

The material to be analysed is treated as follows:

NOTE: Schematic presentations of the analytical procedures are given in Appendix B.

1.5.1 Loss on ignition (see Section 3)

A sample is heated to constant mass at 1100°C and loss of ignition is determined by mass difference.

1.5.2 Determination of silicon, iron, titanium, manganese, chromium, aluminium, calcium and magnesium oxides (see Section 4)

A sample is decomposed with hydrochloric acid. The silicon dioxide is separated by filtration, is ignited, and weighed before and after treatment with hydrofluoric and sulphuric acids. The residue is fused with sodium carbonate and boric acid, and the product is dissolved in the original filtrate. It is then diluted to a standard volume. Aliquots are used for the spectrophotometric determination of residual silicon, iron, titanium, manganese and chromium oxides using respectively ammonium molybdate, 1,10-phenanthroline, hydrogen peroxide, potassium periodate and diphenylcarbazide. If the chromium oxide content is greater than 0.1 percent, the chromium(III)-EDTA method is used. Aluminium oxide is determined volumetrically with EDTA after extraction of interfering elements with cupferron in chloroform. Calcium and magnesium oxides are determined titrimetrically with EGTA and CDTA respectively.

1.5.3 Determination of sodium, potassium and lithium oxides (see Section 5)

A sample is reacted with nitric, perchloric and hydrofluoric acids and then evaporated to dryness. The residue is dissolved in dilute hydrochloric acid and the alkali metal oxides are determined using flame photometry.

1.5.4 Determination of boron in magnesite (see Section 6)

A test sample is extracted with sulphuric acid and the boron is determined spectrophotometrically using carminic acid.

1.6 SAFETY

For information on laboratory safety, reference should be made to the relevant parts of AS/NZS 2243.

Reagents used may be hazardous or toxic and reference should be made to the appropriate Material Safety Data Sheets.

SECTION 2 S A M P L I N G A N D S A M P L E P R E P A R A T I O N

2.1 SCOPE OF SECTION

This Section sets out methods of sampling and subsequent preparation of samples for analysis.

2.2 GROSS SAMPLING

2.2.1 Shaped materials

Methods for obtaining a suitable sample for analytical procedures outlined below are described in AS 2497.1.

2.2.2 Bulk or ground materials

Procedures for the selection of the gross sample are the subject of agreement between contracting parties.

2.3 PREPARATION OF SAMPLE

2.3.1 Crushing

2.3.1.1 *Shaped products*

The procedure shall be as follows:

- (a) Brush shape(s) clean of any loose, extraneous material and cut or break shape(s) into two approximately equal parts.

NOTE: Discard any extraneous materials present as they will give misleading results.

- (b) Completely break up and crush one half of each shape, including any skin (see Note to Step (a)) so that all particles are no greater than 4.00 mm.

NOTE: Care is required in the choice of crushing apparatus so as to ensure that the surfaces of the apparatus which come into contact with the test refractory do not measurably contribute material to the crushed product.

- (c) Reduce the sample mass to about 400 g by mixing, coning and quartering, or by the use of an appropriate sample divider. Crush in an iron mortar to pass a sieve of 2.00 mm apertures or less (see Note to Step (b)).

2.3.1.2 *Bulk or ground materials*

The procedure shall be as follows:

- (a) Mix, cone and quarter, or use a sample divider, to reduce the gross sample to about 400 g.
- (b) Crush, if necessary, as with shaped samples (see 2.3.1.1), to particles of a size which pass a 2.00 mm sieve.

2.3.2 Samples for analysis

2.3.2.1 Preliminary treatment

The procedure shall be as follows:

- (a) Spread a piece of clean white paper over the end of a magnet and slowly pass it backwards and forwards over, and close to, the crushed and/or ground sample spread thinly on a clean smooth surface. Remove and discard (see Note) any particles attached to the magnet from the magnet, remix the sample and repeat the process. Continue until no more iron is removed from the sample.

NOTE: The material to be discarded should be inspected under magnification to ensure that only metallic iron is being discarded.

- (b) Examine residue, under magnification if necessary, to check for freedom from iron particles (e.g. filings, shavings, scrapings) as may have been contributed by machinery used in quarrying, mining, transporting or processing or, if appropriate, by foreign materials with which it came in contact during its service life.
- (c) Mix, cone and quarter, or use a mechanical sample divider, to obtain two portions, A and B, of about 50 g each.

NOTE: In cases where an iron determination is required, the procedure for Portion B (2.3.2.3) should be followed as the hardened steel percussion mortar, used in the procedure for Portion A (2.3.2.2), may introduce significant iron contamination which cannot be removed by a magnet.

2.3.2.2 Portion A—to be used for the main analysis (see Note to 2.3.2.1(c))

The procedure shall be as follows:

- (a) Crush sample in a hardened steel percussion mortar until all particles are not larger than 500 μm .
- (b) Mix, cone and quarter, or use a mechanical sample divider, to obtain a 25 g to 30 g sample.
- (c) Crush this sample in a hardened steel percussion mortar to a maximum particle size of 125 μm and remove any particles of extraneous iron with a magnet as before (see 2.3.2.1(a)).

2.3.2.3 Portion B—to be used where iron determination is required

The procedure shall be as follows:

- (a) Crush in a pure alumina mortar to a maximum particle size of 500 μm .
- (b) Mix, cone and quarter, or use a mechanical sample divider to obtain a 10 g to 15 g sample.
- (c) Grind this sample in a pure alumina mortar to a maximum particle size of 125 μm .

NOTE: A non-metallic sieve (e.g. nylon bolting cloth) is preferred at this stage.

SECTION 3 DETERMINATION OF LOSS ON IGNITION

3.1 SCOPE OF SECTION

This Section sets out the method for determining the loss on ignition of the test sample prepared in accordance with Section 2.

3.2 APPARATUS

The following apparatus is required:

3.2.1 Balance

Capable of weighing the platinum crucible and sample to an accuracy of ± 0.001 g.

3.2.2 Drying oven

Capable of maintaining any set temperature in the range 110°C to 150°C to an accuracy of $\pm 2^\circ\text{C}$.

3.2.3 Muffle furnace

Capable of maintaining any set temperature in the range 1000°C to 1200°C to an accuracy of $\pm 25^\circ\text{C}$.

3.2.4 Platinum crucible

Which has been dried at 1100°C to constant mass (M_c) and stored in a desiccator until required.

3.3 PROCEDURE

The procedure shall be as follows:

- Dry between 10 g and 15 g of the appropriate analysis sample (2.3.2) to constant mass at 110°C.
- Weigh, to the nearest 0.001 g, approximately 1 g of this sample into the dried and weighed platinum crucible (3.2.4).
- Place the crucible in the furnace preset at approximately 200°C and raise the temperature to 1100°C.
NOTE: Alternatively, to reduce the preheating time, the sample may be heated on a low burner, gradually increasing the flame temperature over a period of about 20 min.
- Ignite to constant mass at 1100°C, recording the final mass of crucible and sample.
NOTE: Ignition for 1 h is usually sufficient.
- Calculate the percentage loss on ignition from the following formula to the nearest 0.1 percent:

$$\% \text{ loss on ignition } (m/m) = \frac{100(m_1 - m_2)}{m_1 - M_c}$$

where

M_c = mass of crucible (3.2.4), in grams

m_1 = mass of crucible and sample before ignition, (3.3(b)), in grams

m_2 = mass of crucible and sample after ignition, (3.3(d)), in grams

SECTION 4 DETERMINATION OF SILICON, IRON, TITANIUM, MANGANESE, CHROMIUM, ALUMINIUM, CALCIUM AND MAGNESIUM OXIDES

4.1 SCOPE OF SECTION

This Section sets out methods for determining the silicon, iron, titanium, manganese, chromium, aluminium, calcium and magnesium oxides content of the test sample prepared in accordance with Section 2.

4.2 REAGENTS

4.2.1 General

All reagents shall be analytical reagent grade materials, free from impurities which will significantly contribute to or interfere with the constituents of interest being determined by this method.

Distilled or demineralized water shall be used throughout the analysis.

4.2.2 Solid reagents

4.2.2.1 *Ammonium chloride (NH_4Cl)*

4.2.2.2 *Boric acid (H_3BO_3)*

4.2.2.3 *Potassium periodate (KIO_4)*

4.2.2.4 *Sodium carbonate, anhydrous (Na_2CO_3)*

4.2.3 General solutions and solvents

4.2.3.1 *Acetic acid (500 mL/L)*

Dilute 500 mL concentrated acetic acid (ζ_{20} 1048 kg/m³ to 1050 kg/m³) to 1 L.

CAUTION: ACETIC ACID LIQUID AND VAPOUR ARE CORROSIVE AND IRRITATING TO SKIN AND EYES. DIRECT CONTACT SHOULD BE AVOIDED.

4.2.3.2 *Ammonia solution (ζ_{20} 880 kg/m³)*

CAUTION: AMMONIA GAS IS AN EXTREMELY IRRITATING AND PENETRATING GAS WHOSE SOLUTION IS ALKALINE AND CORROSIVE. DIRECT CONTACT WITH HIGH CONCENTRATIONS OF SOLUTION SHOULD BE AVOIDED.

4.2.3.3 *Ammonia solution (500 mL/L)*

Prepare 500 mL from concentrated ammonia solution (4.2.3.2).

NOTE: See Caution to 4.2.3.2.

4.2.3.4 *Ammonium acetate buffer solution*

Dilute 120 mL concentrated acetic acid (ζ_{20} 1048 kg/m³ to 1050 kg/m³) to 600 mL. Cautiously add 74 mL concentrated ammonia solution (4.2.3.2). Cool and dilute to 1 L.

4.2.3.5 *Ammonium acetate buffer solution (pH 3.8)*

Dilute 5 mL concentrated ammonia solution (4.2.3.2) to 100 mL. Add 30 mL concentrated acetic acid (ζ_{20} 1048 kg/m³ to 1050 kg/m³). Adjust with either reagent, as appropriate, to pH 3.8 then dilute to 200 mL with water.

4.2.3.6 Ammonium acetate buffer solution (pH 6.0 to 6.5)

Dilute 140 mL concentrated acetic acid (ζ_{20} 1048 kg/m³ to 1050 kg/m³) to 1700 mL. Cautiously add 140 mL concentrated ammonia solution (4.2.3.2), cool, mix and adjust the pH range to pH 6.0 to 6.5 with either reagent, as necessary.

4.2.3.7 Ammonium cerium(IV) nitrate solution (10 g/L)

Dissolve 2.5 g ammonium cerium(IV) nitrate, (NH₄)₂Ce(NO₃)₆, in 200 mL water. Cautiously add, with stirring, 7 mL concentrated sulphuric acid (4.2.3.35). Cool and dilute to 250 mL.

4.2.3.8 Ammonium molybdate solution (100 g/L)

Dissolve 50 g ammonium molybdate, (NH₄)₆Mo₇O₂₄·4H₂O, in water, filtering if necessary and dilute to 500 mL. Store in a polyethylene bottle. Discard after 4 weeks, or earlier if any appreciable deposit is observed.

4.2.3.9 Ammonium nitrate solution (10 g/L)

Dilute 10 mL concentrated nitric acid (4.2.3.26) to approximately 200 mL. Add 500 mL/L ammonia solution (4.2.3.3) until the solution is faintly alkaline to bromophenol blue (4.2.5.1). Cool and dilute to 1 L. Heat to 80°C before use.

4.2.3.10 Chloroform.**4.2.3.11 Cupferron solution (60 g/L)**

Dissolve 6 g cupferron (see Note) in cold water, dilute to 100 mL and filter. Prepare immediately before use.

NOTE: If the reagent is discoloured or gives a strongly coloured solution, new stock should be used.

4.2.3.12 Diphenylcarbazide solution (10 g/L)

Dissolve 0.1 g diphenylcarbazide in 10 mL acetone. Prepare just before use.

4.2.3.13 Ethanol or industrial alcohol (950 mL/L)**4.2.3.14 EDTA solution (50 g/L)**

Prepare 500 mL and store in a polyethylene bottle.

4.2.3.15 Flocculating agent (1 g/L)

Prepare 1 L.

NOTE: Alfloc 6751 or equivalent is a suitable agent.

4.2.3.16 Hydrochloric acid (ζ_{20} 1180 kg/m³).

CAUTION: HYDROCHLORIC ACID LIQUID AND FUMES ARE HIGHLY IRRITATING TO EYES, SKIN AND RESPIRATORY PASSAGES AS WELL AS TO MANY METALS.

4.2.3.17 Hydrochloric acid (500 mL/L)

Prepare from concentrated acid (4.2.3.16)

CAUTION: GREAT CARE IS ALWAYS NECESSARY WHEN DILUTING CONCENTRATED ACIDS, AS HEAT GENERATED BY IMPROPER MIXING MAY BE SUFFICIENT TO CAUSE LOCAL BOILING AND RESULT IN THE 'SPITTING' OF HOT ACID DROPLETS. THE RECOMMENDED SAFE PROCEDURE IS TO ADD THE ACID, IN SMALL AMOUNTS, TO THE WATER WITH STIRRING. THE WEARING OF SAFETY GOGGLES OR THE EQUIVALENT IS ALWAYS NECESSARY.

4.2.3.18 *Hydrochloric acid (250 mL/L)*

Prepare from concentrated acid (4.2.3.16). See Caution to Clause 4.2.3.17.

4.2.3.19 *Hydrochloric acid (200 mL/L)*

Prepare from concentrated acid (4.2.3.16). See Caution to Clause 4.2.3.17.

4.2.3.20 *Hydrochloric acid (100 mL/L)*

Prepare from concentrated acid (4.2.3.16). See Caution to Clause 4.2.3.17.

4.2.3.21 *Hydrochloric acid (50 mL/L)*

Prepare from concentrated acid (4.2.3.16). See Caution to Clause 4.2.3.17.

4.2.3.22 *Hydrofluoric acid (ζ_{20} 1130 kg/m³).*

WARNING: HYDROFLUORIC ACID IS EXTREMELY CORROSIVE AND TOXIC BOTH AS VAPOUR AND SOLUTION, AND ITS EFFECTS MAY NOT BE IMMEDIATELY APPARENT. IT SHOULD ONLY BE USED IN A VENTILATED FUME CUPBOARD. DIRECT CONTACT SHOULD BE AVOIDED UNDER ALL CIRCUMSTANCES.

4.2.3.23 *Hydrogen peroxide solution (60 g/L)*

Dilute 200 mL hydrogen peroxide (300 g/L) to 1 L.

4.2.3.24 *Hydroxylammonium chloride solution (100 g/L)*

Dissolve 10 g hydroxylammonium chloride in warm water, filtering if necessary. Cool and dilute to 100 mL.

4.2.3.25 *Magnesium sulphate solution (0.2 g MgO/100 mL)*

Prepare 500 mL of filtered solution using 6.11 g magnesium sulphate heptahydrate, MgSO₄·7H₂O.

4.2.3.26 *Nitric acid (ζ_{20} 1420 kg/m³)*

CAUTION: NITRIC ACID IS AN EXTREMELY CORROSIVE, OXIDIZING ACID WHICH ACTS RAPIDLY ON CONTACT WITH LIVING TISSUE. ITS FUMES ARE CORROSIVE AND POISONOUS AND DIRECT CONTACT SHOULD BE AVOIDED.

4.2.3.27 *1,10-Phenanthroline solution (10 g/L)*

Prepare sufficient for immediate use by dissolving in 500 mL/L acetic acid (4.2.3.1).

4.2.3.28 *Phosphoric acid (400 mL/L)*

Prepare 1 L from concentrated phosphoric acid (ζ_{20} 1750 kg/m³). See Caution to 4.2.3.17.

4.2.3.29 *Phosphoric acid (100 mL/L)*

Prepare 1 L from concentrated phosphoric acid (ζ_{20} 1750 kg/m³). See Caution to 4.2.3.17.

4.2.3.30 *Polyethylene glycol solution (2.5 g/L)*

Make up 200 L from a high molecular weight ($\geq 35\,000$) polyethylene glycol. Discard after two weeks.

NOTE: As the glycol is difficult to dissolve, prolonged mechanical stirring may be required.