BS EN 14368:2015

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# Products used for treatment of water intended for human consumption — Manganese dioxide coated limestone

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**National foreword**

This British Standard is the UK implementation of EN 14368:2015. It supersedes BS EN 14368:2003 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment.

A list of organizations represented on this committee can be obtained on request to its secretary.

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EUROPEAN STANDARD

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# EN 14368

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English Version

# Products used for treatment of water intended for human consumption - Manganese dioxide coated limestone

Produits utilisés pour le traitement de l'eau destinée à la consommation humaine - Carbonate de calcium revêtu de dioxyde de manganèse

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Mit Mangandioxid beschichteter Kalkstein

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**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

# Contents

# Foreword

This document (EN 14368:2015) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2015, and conflicting national standards shall be withdrawn at the latest by October 2015.

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This document supersedes EN 14368:2003.

The main technical difference between this edition and EN 14368:2003 is the updating of 9.2 in line with current legislation.

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# Introduction

In respect of potential adverse effects on the quality of water intended for human consumption, caused by the product covered by this European Standard:

a) this European Standard provides no information as to whether the product may be used without restriction in any of the Member States of the EU or EFTA;

b) it should be noted that, while awaiting the adoption of verifiable European criteria, existing national regulations concerning the use and/or the characteristics of this product remain in force.

NOTE Conformity with this standard does not confer or imply acceptance or approval of the product in any of the Member States of the EU or EFTA. The use of the product covered by this European Standard is subject to regulation or control by National Authorities.

# 1 Scope

This European Standard is applicable to manganese dioxide coated limestone used for treatment of water intended for human consumption. It describes the characteristics of manganese dioxide coated limestone and specifies the requirements and the corresponding test methods for manganese dioxide coated limestone. It gives information on its use in water treatment.

# 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1018, *Chemicals used for treatment of water intended for human consumption — Calcium carbonate*

EN 12901:1999, *Products used for treatment of water intended for human consumption — Inorganic supporting and filtering materials — Definitions*

EN 12902, *Products used for treatment of water intended for human consumption — Inorganic supporting and filtering materials — Methods of test*

EN 13752, *Products used for treatment of water intended for human consumption — Manganese dioxide*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

ISO 6333, *Water quality — Determination of manganese — Formaldoxime spectrometric method*

# 3 Terms, definitions and symbols

For the purposes of this document, the terms, definitions and symbols given in EN 12901:1999 apply.

# 4 Description

## 4.1 Identification

### 4.1.1 Chemical name

Manganese dioxide on limestone support material.

### 4.1.2 Synonyms or common names

Manganese (IV) oxide, pyrolusite on limestone support material.

### 4.1.3 Chemical formula

$MnO_2$ and $CaCO_3$.

#### 4.1.4 CAS Registry number[1)]

Manganese dioxide: 1313-13-9.

Calcium carbonate: 471-34-1.

#### 4.1.5 EINECS reference[2)]

Manganese dioxide: 215-202-6.

Calcium carbonate: 207-439-9.

### 4.2 Commercial form

Manganese dioxide coated limestone is a granular material available in different particle size ranges.

## 5 Physical properties

### 5.1 Appearance

The product is a granular material varying in colour from dark grey to black.

The product shall be generally homogeneous and shall be visibly free of extraneous matter.

### 5.2 Particle size distribution

The particle size distribution shall be described by either:

a)

— effective size: ($d_{10}$) with a maximum deviation of ± 5 %;

— uniformity coefficient: ($U$) less than 2,0;

— minimum size: ($d_1$) with a maximum deviation of ± 5 %.

or

b) particle size range and mass fraction of oversize and undersize particles according to application.

The maximum contents of oversize and undersize shall be a mass fraction of 5 % for the application of the product in multimedia filters and a mass fraction of 10 % for use in single media filters. See A.2.3 for examples of available particle sizes that are used.

NOTE 1 The particle size can decrease during transportation and handling.

NOTE 2 Other values can be necessary for certain applications.

### 5.3 Density

#### 5.3.1 Bulk density loose

The bulk density loose shall be in the range of 1 500 kg/m$^3$ to 1 700 kg/m$^3$.

1) Chemical Abstracts Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

#### 5.3.2 Bulk density packed

The bulk density packed shall be in the range of 1 700 kg/m$^3$ to 1 900 kg/m$^3$.

## 6 Chemical properties

This European Standard specifies the minimum purity requirements for manganese dioxide coated limestone used for the treatment of water intended for human consumption. Limits are given for impurities commonly present in the product. Depending on the raw material and the manufacturing process other impurities may be present and, if so, this shall be notified to the user and when necessary to relevant authorities.

Users of this product should satisfy themselves that it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, contents of other impurities and additives used in the products not stated in the product standard, and other relevant factors.

Limits have been given for impurities and chemical parameters where these are likely to be present in significant quantities from the current production process and raw materials. If the production process or raw materials lead to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

The chemical composition of the product is not relevant to its performance. The chemical composition of the components is given in EN 1018 and EN 13752.

After filling, washing and commissioning of a filter system producing drinking water, manganese dioxide coated limestone should not increase the concentrations of chemical parameters (see [1]).

NOTE Water extractable substances, determined in accordance with the method for granular materials given in EN 12902, can be used to estimate the leaching of the chemicals specified in EN 12902.

## 7 Specific properties

The oxidation capacity shall be at least 500 bed volumes when tested according to the method described in 8.2.4.

## 8 Test methods

### 8.1 Sampling

Prepare the laboratory sample required by the relevant procedure described in EN 12902.

### 8.2 Analysis

#### 8.2.1 Particle size distribution

The particle size distribution shall be determined on samples taken at the point of manufacture using the method of test given in EN 12902.

#### 8.2.2 Bulk density loose

The bulk density loose shall be determined in accordance with EN 12902.

#### 8.2.3 Bulk density packed

The bulk density packed shall be determined in accordance with EN 12902.

### 8.2.4 Oxidation capacity

#### 8.2.4.1 Principle

A solution of manganese sulfate is passed through a bed of “regenerated” manganese dioxide coated limestone. Portions of the effluent are analysed for manganese and the cumulative volume, until breakthrough of manganese, is determined.

#### 8.2.4.2 Reagents

##### 8.2.4.2.1 General

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 2 in accordance with EN ISO 3696.

**8.2.4.2.2 Potassium permanganate**, solution 3,0 g/l

Dissolve 6,0 g of potassium permanganate ($KMnO_4$) in 2 l of water. Decant the clear solution and store in a dark bottle.

**8.2.4.2.3 Manganese sulfate**, solution 5 mg/l

Dissolve 1,00 g of sodium hydrogen carbonate ($NaHCO_3$) in water and add 0,1538 g of manganese sulfate monohydrate ($MnSO_4.H_2O$). Dilute to 10 l with water and adjust the pH to 7,0 ± 0,5 using dilute sulfuric acid or sodium hydroxide solution as required.

#### 8.2.4.3 Apparatus

##### 8.2.4.3.1 General

Ordinary laboratory apparatus and glassware together with the following.

**8.2.4.3.2** Glass or transparent plastic column, length 1,00 m, inside diameter 25 mm, equipped with a flow control valve at its base.

**8.2.4.3.3** Graduated measuring cylinder, 200 ml capacity.

**8.2.4.3.4** Borosilicate glass bottle, 10 l capacity.

#### 8.2.4.4 Procedure

##### 8.2.4.4.1 Regeneration of material

Measure 300 ml of packed manganese dioxide coated limestone granules with the measuring cylinder (8.2.4.3.3), and place them in the column (8.2.4.3.2).

Connect the outlet of the column to a cold water tap by means of suitable flexible tubing and backwash the granules with a water flow sufficient to fluidize the bed. Allow the granules to settle and regenerate the manganese dioxide coated limestone by running 2 l of potassium permanganate solution (8.2.4.2.2) through the column with a flow rate of about 500 ml/h. Rinse carefully with water until complete disappearance of the pink colour.

##### 8.2.4.4.2 Determination

Run the manganese sulfate solution (8.2.4.2.3) at a flow rate of 5 l/h through the column and collect the effluent in separate fractions of 200 ml each. Analyse the fractions for manganese in accordance with ISO 6333 and stop the manganese sulfate solution flow when the concentration of manganese in the effluent is higher than 0,05 mg/l.

Reject this last fraction and note the total volume of the manganese-free water discharged from the column.

Repeat the run including the regeneration step three times, each time using the same manganese dioxide coated limestone sample. Note the volume of manganese-free water collected in each test.

#### 8.2.4.5 Expression of results

The oxidation capacity of manganese dioxide coated limestone, $C$, expressed as bed volumes of test solution treated, is given by the following formula:

$$C = \frac{V}{V_1} \quad (1)$$

where

$V$ is the mean volume, in litres, of water with a manganese content less than 0,05 mg/l in the four runs;

$V_1$ is the volume, in litres, of the bed of manganese dioxide coated limestone.

## 9 Labelling, transportation and storage

### 9.1 Means of delivery

Manganese dioxide coated limestone shall be delivered in bags of 25 kg to 50 kg. Because of the relative softness of the material it is not recommended that bulk bags be used.

In order that the purity of the product is not affected, the means of delivery shall not have been used previously for any different product or it shall have been specially cleaned and prepared before use.

### 9.2 Labelling according to the EU legislation

The following labelling requirements shall apply to manganese dioxide coated limestone at the date of publication of this standard.

| Hazard pictogram | — Signal word:<br>**Warning**<br>— Hazard statements:<br>H302: Harmful if swallowed<br>H332: Harmful if inhaled |
|---|---|
|  | |

**Figure 1 — GHS07**

The legislation [2] contains a list of substances classified by the EU. Substances not listed in this regulation should be classified on the basis of their intrinsic properties according to the criteria in the Regulation by the person responsible for placing the product on the market.

### 9.3 Transportation regulations and labelling

Manganese dioxide coated limestone is not listed under a UN number [3]; it is not a dangerous cargo.

## 9.4 Marking

The marking shall include the following:

— name “manganese dioxide coated limestone”, trade name and grade;

— net mass;

— name and the address of the supplier and/or manufacturer;

— statement “This product conforms to EN 14368”.

## 9.5 Storage

### 9.5.1 Long term chemical stability

Manganese dioxide coated limestone can be stored for an unlimited period of time.

### 9.5.2 Storage incompatibility

Manganese dioxide coated limestone shall not be allowed to come into contact with hydrochloric acid; contact with hydrochloric acid produces chlorine gas. Avoid storing with any chloride salt jointly with an acid, or hydrogen sulfates.

# Annex A
(informative)

# General information on manganese dioxide coated limestone

## A.1 Origin

### A.1.1 Raw material

The raw materials are manganese dioxide in accordance with EN 13752, which is suitable for use as catalytic filtration material, and calcium carbonate in accordance with EN 1018. The catalytic activity of manganese dioxide varies greatly and is generally unrelated to its manganese content.

### A.1.2 Manufacturing process

Manganese dioxide coated limestone is produced by granulation of manganese dioxide on calcium carbonate support material using a thin layer of calcium hydroxide to promote adhesion.

## A.2 Typical properties

### A.2.1 Chemical composition

The chemical composition of the product depends on the composition of the two components (see EN 13752 and EN 1018).

### A.2.2 Mechanical strength

The mechanical strength of manganese dioxide coated limestone is low.

Abrasion products consist of dust and small particles of material. They are formed during transportation, filling, and washing. Abrasion products are not completely removed by washing and attempting to do so can result in the generation of excessive fines as a result of attrition with sand particles if a mixed bed of sand and manganese dioxide coated limestone is washed too vigorously. When washing beds containing manganese dioxide coated limestone the bed should be expanded to a just-fluidized condition and no more.

The existing methods for determination of abrasion do not lead to exact results regarding the behaviour of filter media during operation. They can be used for comparison of different filter media.

### A.2.3 Alternative description of particle size distribution

Examples of particle size distribution described by different particle size ranges and a permissible mass fraction of oversize and undersize product are given in Table A.1.

**Table A.1 — Examples of particle size ranges**

| **Particle size range** (mm) | **Permissible mass fraction, %** | |
|---|---|---|
| | **Undersize** | **Oversize** |
| 0,7 to 1,2 | 5 | 5 |
| 1,0 to 3,0 | 10 | 10 |
| 2,0 to 4,0 | 10 | 10 |

Other particle size ranges can be specified.

## A.3 Use

### A.3.1 Function

Manganese dioxide coated limestone is used as a catalytic filtering medium for the removal of iron and manganese from water.

Manganese dioxide coated limestone can be used alone or in combination with sand.

### A.3.2 Oxidation capacity

Manganese dioxide coated limestone will remove iron from water provided there is sufficient oxygen present (60 % oxygen saturation); this process makes no demand on the manganese dioxide and will continue indefinitely provided the precipitated iron hydroxide is removed from the surface of the manganese oxide coated limestone.

Manganese removal is achieved ideally in the presence of chlorine or strong oxidizing agent and, given a sufficient concentration of oxidizing agent, will continue indefinitely. In the absence of a strong oxidizing agent the manganese dioxide will itself act as an oxidizing agent and oxidize manganese in the water until the surface of the manganese dioxide coated limestone has been reduced to an inactive lower oxidation state. This fact is utilized in determining the oxidation capacity of manganese dioxide coated limestone (see 8.2.4).

### A.3.3 Amount used

The specific amount of manganese dioxide coated limestone used depends upon the application.

### A.3.4 Means of application

Manganese dioxide coated limestone is used in open or closed single or multilayer filters as an addition to silica sand with which it should mix intimately and not form a discrete layer.

Manganese dioxide coated limestone is not suitable for the treatment of water having a pH lower than approximately 6,5 unless the pH is adjusted.

### A.3.5 Secondary effects

When treating water which contains more than approximately 0,2 mg/l manganese, the sand in which the manganese dioxide coated limestone is distributed can become coated with a deposit of manganese dioxide. This occurs as a result of there being more manganese dioxide deposited from the water being treated during the filtration stage than is lost by attrition during the backwash stage. In consequence of this, the density of the sand will increase with consequent increase in energy required for backwashing the bed. The sand/manganese dioxide coated limestone mixture will also increase in particle size and media can have to be removed from the bed in order to avoid exceeding the maximum level. In waters with very low concentrations of manganese the reverse process occurs and more manganese dioxide is lost through attrition during backwashing than is deposited during manganese removal. As a consequence the manganese dioxide coated limestone can require topping-up periodically in filters treating such waters.

## A.4 Hydraulic characteristics

### A.4.1 Interstitial volume

The interstitial volume is approximately 0,4 volume fraction. If used for calculations the interstitial volume should be measured.

### A.4.2 Headloss in filtration

Head loss depends on size, shape and roughness of particles, filtration rate, filter bed depth, and water temperature.

### A.4.3 Expansion in up-flow washing

The expansion during washing depends on flow rate, effective size, density, shape and roughness of particles, and water temperature.

The backwash regime used for filters containing manganese dioxide coated limestone should not cause undue attrition of the manganese dioxide coated limestone; generally the lowest possible backwash velocity consistent with bed fluidization should be used.

# Annex B
(normative)

# General rules relating to safety

## B.1 Rules for safe handling and use

The supplier shall provide current safety instructions.

## B.2 Emergency procedures

### B.2.1 First aid

In case of contact with skin, wash with soap and water.

In case of contact with eyes, flush with plenty of water.

In case of inhalation, move to fresh air.

### B.2.2 Spillage

Sweep and discard in refuse container. Avoid mixing with combustible materials.

NOTE Local regulations might apply to the disposal of this product.

### B.2.3 Fire

No special requirements apply.

# Bibliography

[1] 98/83/EC, Council Directive of 3 November 1998 on the quality of water intended for human consumption

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (REACH)

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