BS EN 12911:2013

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Products used for treatment of water intended for human consumption — Manganese greensand

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National foreword

This British Standard is the UK implementation of EN 12911:2013. It supersedes BS EN 12911:2006 which is withdrawn.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.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Products used for treatment of water intended for human consumption - Manganese greensand

Produits utilisés pour le traitement de l'eau destinée à la consommation humaine - Sable vert manganisé

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Mangangrünsand

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Foreword

This document (EN 12911:2013) 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of an identical text or by endorsement, at the latest by November 2013, and conflicting national standards shall be withdrawn at the latest by November 2013.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 12911:2006.

Significant technical difference between this edition and EN 12911:2006 is as follows:

— Updating of subclause 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, the following statements apply:

— 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.

— 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 European Standard does not confer or imply acceptance or approval of the product in any of the Member States of the EU or EFTA. 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 greensand used for the treatment of water intended for human consumption. It describes the characteristics of manganese greensand and specifies the requirements and the corresponding test methods for manganese greensand. 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 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 ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

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

ISO 9682-1:2009, *Iron ores — Determination of manganese content — Part 1: Flame atomic absorption spectrometric method*

3 Terms and definitions and symbols

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

4 Description

4.1 Identification

4.1.1 Chemical name(s)

Manganese oxide coated zeolite (glauconite).

NOTE The product is a preparation.

4.1.2 Synonym or common names

Manganese greensand, manganese zeolite, ferro-sand, greensand.

4.1.3 Chemical formula

Not applicable.

4.1.4 CAS Registry Number[1)]

Glauconite: 90387-66-9.

Manganese oxide: 1313-13-9.

4.1.5 EINECS reference[2)]

Glauconite: 291-341-6.

Manganese oxide: 215-202-6.

4.2 Commercial form

Manganese greensand is a granular product available in only one particle size range.

5 Physical properties

5.1 Appearance

The product comprises dry, sand-like, free flowing black granules. The particles are coated with a black manganese dioxide coating. The product has a granular shape, dense crystalline structure and a rough texture.

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 determined on samples taken at the point of manufacture using the test method given in EN 12902.

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

The particle size distribution shall be described by either:

a) effective size: (d_{10}) 0,30 mm to 0,35 mm with a maximum deviation of ± 0,03 mm;

   1) uniformity coefficient: (U) shall be less than 1,6;

   2) minimum size: (d_1) shall be at least 0,25 mm;

   3) maximum size: shall not exceed 1,25 mm;

or

b) by particle size range and by mass fraction of oversize and undersize particles.

The maximum permitted mass fractions of oversize and undersize are 5 %.

NOTE 2 Other values might be necessary for certain applications.

1) Chemical Abstracts Service Registry Number.
2) European Inventory of Existing Commercial Chemical Substances.

5.3 Density (bulk density loose)

The bulk density loose shall be at least 1 300 kg/m^3.

6 Chemical properties

This European Standard specifies the minimum purity requirements for manganese greensand 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, the user, and when necessary the relevant authorities, shall be notified.

Users of this product should check the national regulations in order to clarify whether 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 product not stated in this product standard.

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 the presence of significant amounts of impurities, by-products or additives being present, the user shall be notified.

The composition of the commercial product shall conform to Table 1.

Table 1 — Composition of commercial product

Parameters		Limit in mass fraction %
Manganese oxides (as Mn)[a]		0,2 to 0,8
Mass loss at 150 °C	max.	6
Ignition loss at 650 °C	max.	8
[a] The manganese in the product is present as a mixture of different oxides.		

NOTE 1 Acid-soluble material is not a relevant parameter for this product, which is not stable to acids and which will react with hydrochloric acid releasing chlorine gas.

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

NOTE 2 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 of manganese greensand (regenerated form), expressed as grams of Mn per litre of packed product, shall be at least 0,7 g/l.

8 Test methods

8.1 Sampling

Prepare the laboratory sample(s) required by the relevant procedures described in EN 12902.

8.2 Analysis

8.2.1 Particle size distribution

The particle size distribution shall be determined in accordance with EN 12902.

8.2.2 Bulk density loose

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

8.2.3 Mass loss at 150 °C

8.2.3.1 General

The mass loss shall be determined by the method for water content, heating to 150 °C, in accordance with EN 12902.

8.2.3.2 Precision

The absolute difference between two single test results, obtained under repeatability conditions, shall not exceed the repeatability limit, r, in more than one in twenty cases.

$$r = 0{,}07 \times X_1 \quad (1)$$

where

X_1 is the measured value.

8.2.4 Ignition loss at 650 °C

8.2.4.1 Principle

The sample is heated to constant mass at 650 °C. It is assumed that water, including chemically bound water, is the only material present in the manganese greensand that is volatile at this temperature.

At 650 °C, the loss of water is practically complete.

8.2.4.2 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

8.2.4.2.1 Muffle furnace, capable of being controlled at (650 ± 25) °C.

8.2.4.2.2 High temperature metal or ceramic crucible with lid.

8.2.4.2.3 Desiccator.

8.2.4.2.4 Analytical balance, having an accuracy of ± 0,1 mg.

8.2.4.3 Procedure

Ignite the crucible and the lid (8.2.4.2.2) in the muffle furnace at (650 ± 25) °C for 1 h. Place the crucible and the lid in the desiccator; cool to room temperature and weigh to the nearest 0,1 mg. Note the mass m_0.

Place a 5 g to 10 g sample of manganese greensand into the pre-ignited crucible. Close the crucible and weigh immediately to the nearest 0,5 mg (m_1). Remove the lid and place the crucible and lid in the muffle furnace at (650 ± 25) °C and leave for 3 h. Place the crucible in the desiccator, cover it with the lid and allow to cool to room temperature. When cool, weigh to the nearest 0,5 mg (m_2).

8.2.4.4 Expression of results

The ignition loss, X_2, expressed as a percentage mass fraction of dried product, is given by the following formula:

$$X_2 = \frac{100 \times \left(m_1 - m_2 \right)}{\left(m_1 - m_0 \right)} \quad (2)$$

where

m_0 is the mass, in grams, of the empty crucible and lid;

m_1 is the mass, in grams, of the crucible and lid plus the sample;

m_2 is the mass, in grams, of the crucible and lid plus the ignited sample.

8.2.4.5 Precision

The absolute difference between two single test results, obtained under repeatability conditions, shall not exceed the repeatability limit, r, in more than one in twenty cases.

$$r = 0{,}07 \times X_2 \quad (3)$$

8.2.5 Manganese content

8.2.5.1 Principle

Determination of manganese in accordance with ISO 9682-1:2009, 7.5.1.1, adopting the decomposition procedure "a" (alkali fusion) and using a modified background solution.

8.2.5.2 Background solution

8.2.5.2.1 Reagents

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

8.2.5.2.1.1 Silicon dioxide (SiO_2), powder.

8.2.5.2.1.2 Iron oxide (Fe_2O_3), powder with manganese content less than a mass fraction of 0,003 %.

8.2.5.2.1.3 Aluminium oxide (Al_2O_3), powder.

8.2.5.2.1.4 Sodium carbonate (Na_2CO_3), anhydrous.

8.2.5.2.1.5 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

8.2.5.2.1.6 Hydrochloric acid.

Add a volume of concentrated hydrochloric acid (ρ = 1,18 g/ml) to an equal volume of water.

8.2.5.2.2 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

8.2.5.2.2.1 Muffle furnace, capable of being controlled at 1 000 °C to 1 050 °C.

8.2.5.2.2.2 Platinum crucible.

8.2.5.2.2.3 Magnetic stirrer hotplate.

8.2.5.2.2.4 Oven, capable of being controlled at (150 ± 5) °C.

8.2.5.2.3 Preparation

Mix carefully in a platinum crucible (8.2.5.2.2.2) 2,120 g of silicon dioxide (8.2.5.2.1.1), 0,96 g of iron oxide (8.2.5.2.1.2), 0,32 g of aluminium oxide (8.2.5.2.1.3), 32 g of sodium carbonate (8.2.5.2.1.4) and 16 g of sodium tetraborate (8.2.5.2.1.5). Melt in the muffle furnace (8.2.5.2.2.1) for 30 min. Allow to cool gently to room temperature, swirling the melt as it solidifies. Place a polytetrafluoroethylene (PTFE) coated stirring bar in the crucible and place the crucible in a squat-form beaker. Add 200 ml hydrochloric acid (8.2.5.2.1.6), cover and heat while stirring on a magnetic stirrer hotplate (8.2.5.2.2.3) until dissolution of the melt is complete. Transfer the solution to a 1 000 ml volumetric flask, dilute to volume with water and mix. The solution is stable for a few days; discard if a precipitate appears.

8.2.5.3 Procedure

Pre-dry the test sample at (150 ± 5) °C. Weigh to the nearest 0,002 g approximately 0,1 g of the pre-dried sample; this constitutes the "test portion".

Proceed in accordance with ISO 9682-1:2009, following the alkali fusion method for decomposition, and employing the background solution (8.2.5.2).

8.2.6 Oxidation capacity

8.2.6.1 Principle

A solution of manganese sulfate is run through a bed of "regenerated" manganese greensand. Portions of the effluent are analysed for manganese and the cumulative volume until breakthrough of manganese is determined.

8.2.6.2 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

8.2.6.2.1 Glass or transparent plastic column.

The column shall be of length 1,00 m and of inside diameter 25 mm, equipped with a flow control valve at its base.

8.2.6.2.2 Graduated measuring cylinders, of capacity 200 ml.

8.2.6.2.3 Graduated measuring cylinder, of capacity 500 ml.

8.2.6.2.4 Borosilicate glass bottle, of capacity 10 l.

8.2.6.3 Reagents

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

8.2.6.3.1 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.

8.2.6.3.2 Manganese sulfate solution, 10 mg/l Mn.

Dissolve 1,00 g of sodium hydrogen carbonate ($NaHCO_3$) and subsequently 0,307 6 g of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) in several litres of water. Dilute to 10 l with water in the glass bottle (8.2.6.2.4). The pH value of the solution shall be between 6 and 7. If necessary, adjust the pH value by adding a diluted solution of sulfuric acid or of sodium hydroxide as appropriate.

8.2.6.4 Procedure

8.2.6.4.1 Manganese greensand regeneration

Measure 300 ml of packed manganese greensand granules with the measuring cylinder (8.2.6.2.3) and place them in the column (8.2.6.2.1).

Backwash the granules with a water flow sufficient to fluidise the bed. Allow the granules to settle and regenerate the manganese greensand, running 2 l of $KMnO_4$ solution (8.2.6.3.1), through the column with a flow rate of about 500 ml/h. Rinse carefully with water until the pink colour completely disappears.

8.2.6.4.2 Determination

Feed the $MnSO_4$ solution (8.2.6.3.2) at a flow rate of 5 l/h to 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 $MnSO_4$ 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 greensand sample. Note the volumes of manganese-free water collected in each test.

8.2.6.5 Expression of results

The manganese greensand oxidation capacity, C, expressed as grams of Mn removed by one litre of product, is given by the formula:

$$C = \frac{V \times 0{,}010}{0{,}3} \qquad (4)$$

where

V is the mean volume of the Mn free water in litres, discharged from the column in the three runs;

0,010 is the Mn concentration of the $MnSO_4$ solution, expressed in grams per litre;

0,3 is the volume, in litres, of the manganese greensand sample.

9 Labelling, transportation and storage

9.1 Means of delivery

Manganese greensand shall be delivered in bags (of plastics materials), or in semi-bulk containers.

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[3)]

Manganese greensand is not listed within Annex VI of Regulation (EC) No 1272/2008 at the date of publication of this European Standard.

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 the marketing of the substance.

9.3 Transportation regulations and labelling

Manganese greensand is not classified as a dangerous product for road, rail, sea, or air transportation. Manganese greensand is not listed under a UN number[4)].

9.4 Marking

The marking shall include the following:

— the name "manganese greensand", trade name and grade;

— the batch number;

— the net mass;

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

— the statement "this product conforms to EN 12911".

9.5 Storage

9.5.1 Long-term stability

If properly stored the manganese greensand is stable indefinitely.

9.5.2 Storage incompatibility

The manganese greensand shall be kept away from hydrochloric acid; when in contact with this chemical, gaseous chlorine is produced.

3) See [2].
4) United Nations Number.

Annex A
(informative)

General information on manganese greensand

A.1 Origin

A.1.1 Raw material

Natural zeolite "glauconite" and manganese dioxide.

A.1.2 Manufacturing process

After mining, the glauconite is screened to obtain a product with the effective size of 0,3 mm to 0,35 mm. After washing with clean water, the granules are treated separately, in sequence, with manganese sulfate and potassium permanganate solutions to form a thin layer of manganese dioxide which adheres to the granules because of the ion exchange capacity of the glauconite. The product is then dried to a free-flowing consistency and bagged for shipment.

A.2 Typical properties

A.2.1 Chemical composition

The typical chemical composition of the manganese greensand is given in Table A.1:

Table A.1 — Chemical composition of the manganese greensand

Parameter	Mass fraction %
SiO_2	52,6
Fe_2O_3	16,9
Al_2O_3	8,0
K_2O	7,0
FeO	3,2
MgO	3,4
Manganese oxides (MnO_2)[a]	0,8
Ignition loss	7,0
[a] The manganese in the product is present as a mixture of different oxides.	

The content of chemical parameters should not exceed the limits given in Table A.2.

Table A.2 — Chemical parameters

Element	Content in mg/kg
Arsenic (As)	25
Cadmium (Cd)	2
Chromium (Cr)	60
Mercury (Hg)	0,1
Nickel (Ni)	25
Lead (Pb)	5
Antimony (Sb)	5
Selenium (Se)	25

A.2.2 Mechanical strength

The mechanical strength of manganese greensand is high. The particle hardness influences the condition of the filter medium in service. Softening of the filter medium is possible in certain circumstances and could require additional chemical feeds.

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.

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

A.2.3 Density

A.2.3.1 Absolute density

The absolute density is approximately 2,4 g/cm^3 (glauconite).

A.2.3.2 Particle density dry

The particle density dry is generally in the range of 1,30 g/cm^3 to 1,42 g/cm^3.

A.2.3.3 Particle density wet

The particle density wet is generally in the range of 1,76 g/cm^3 to 1,94 g/cm^3.

A.2.3.4 Bed density

The bed density is approximately 1 350 kg/m^3 (up-washed and drained).

A.2.4 Porosity of particles

The porosity of particles determined by mercury porosimetry is approximately a volume fraction of 15 %.

A.3 Use

A.3.1 Function

The primary function of manganese greensand is the removal of iron, manganese and hydrogen sulfide from water. It can produce, if the recommended operating conditions are followed correctly, maximum residual iron and manganese contents lower than 0,2 mg/l and 0,05 mg/l respectively. When used for iron removal, manganese dioxide will be reduced and the filter should have sufficient capacity to remove the reduced manganese, or an oxidising agent, such as chlorine or potassium permanganate, will need to be added. Manganese greensand is not suitable for treatment of water having a pH value lower than approximately 6,2 unless the pH value is adjusted.

In addition, the use of manganese greensand offers the following practical properties:

— catalytic activity in oxidation reactions due to the presence of chlorine, permanganate, oxygen;

— filtering capability.

A.3.2 Specific amount

The amount of manganese greensand used depends on application. The manganese greensand is an oxidation catalyst. Theoretically, its life should be unlimited, but in practice it is strictly connected with the ageing due to possible abrasion and physical stress and iron and/or manganese fouling.

A.3.3 Means of application

The manganese greensand is normally used in vertical and horizontal pressure filters as well as open gravity filter systems. The possible methods of application are:

— with continuous regeneration; or

— with intermittent regeneration.

For the practical details about the methods of use, the manufacturer's literature should be consulted.

The product is shipped in a NOT-regenerated form. It is necessary prior to use to regenerate it with a potassium permanganate solution, contacting the bed for a minimum of 4 h. A regeneration level of 4 g of potassium permanganate per litre is recommended.

A.3.4 Secondary effects

The product has no secondary effects.

A.4 Hydraulic characteristics

A.4.1 Interstitial volume

The interstitial volume of the bed after up-washing is approximately 0,3 (*V/V*) to 0,35 (*V/V*). If used for calculations, the interstitial volume should be measured.

A.4.2 Head loss in filtration

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

A.4.3 Expansion during up-flow washing

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

A.5 Rules for safe handling and use

In handling dry manganese greensand, it is recommended to avoid formation of dust and to wear a dust mask.

Threshold Limit Value (ACGIH): Time Weighted Average 5 mg/m^3 expressed as Mn/m^3 air (ceiling value for Mn, powder and compounds)[5)].

A.6 Emergency procedures

A.6.1 First aid

In case of contact with skin there is no danger; it is recommended to wash with water.

In case of contact with eyes, it is recommended to flush with plenty of water.

In case of inhalation, it is recommended to move to fresh air. The person should be treated for dust inhalation.

A.6.2 Spillage

It is recommended to collect and to remove any spillage of solid. Disposal should be in accordance with local regulations.

A.6.3 Fire

The product is not flammable or combustible. There are no restrictions on extinguishing media in fire situations.

5) American Conference of Governmental Industrial Hygienists.

Bibliography

[1] Council Directive 98/83/EC 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

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