# REPORT OF THE AD HOC WORKING GROUP[1] ON THE TECHNOLOGICAL ASSESSMENT OF NATURAL MINERAL WATER TREATMENTS

## ON

# THE EVALUATION OF TREATMENT BY MANGANESE AND IRON OXIHYDROXIDES MEDIA FOR THE REMOVAL OF MANGANESE , IRON AND ARSENIC FROM NATURAL MINERAL WATERS AND SPRING WATERS

**This report does not necessarily reflect the views of the Commission services**

**MARCH 2007**

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[1] The Ad Hoc Working group on the technological assessment of natural mineral water treatment has been set up by the European Commission and agreed by the Member States at the Standing Committee on the Food Chain and Animal Health on 23 June 2005.

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# REPORT ON THE EVALUATION OF TREATMENT BY MANGANESE AND IRON OXIHYDROXIDES MEDIA FOR THE REMOVAL OF MANGANESE, IRON AND ARSENIC FROM NATURAL MINERAL WATERS AND SPRING WATERS

## I) LEGAL FRAMEWORK

### I.1 E.U. definition of natural mineral waters

A natural mineral water (NMW) as defined by Directive 80/777/EEC can be clearly distinguished from ordinary drinking water:
- by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects;
- by its original state which has to be suitable at source for human consumption.

NMW sources have to be continuously kept free from any environmental contamination (microbiological and chemical contaminants) because of their underground origin and the required measures of protection of the sources. Therefore, treatments for the removal of a microbiological or chemical contamination are not allowed by the E.U. N.M.W. legislation.

### I.2 Provisions applicable to NMW treatments

However, a limited number of treatments may be used for technological or food safety purposes. These treatments aim at the removal of:

- Unstable elements such as iron, manganese, sulphur compounds for technological purposes.
- Certain substances, which are naturally, present in NMW but may have an adverse effect on public health if their concentration is above certain levels.

Commission Directive 2003/40/EC has laid down harmonised maximum limits for 15 undesirable constituents, which entered into force from 1st January 2006 (except for fluoride and nickel from 1st January 2008).

Only NMW which comply with these maximum limits may be marketed in the E.U. Others need either to be withdrawn from the market or to be treated with authorised treatments in application to Article 4 of Directive 80/777/EEC, as amended by Directive 96/70/EC.

Where these maximum limits are exceeded and only for naturally present substances, operators shall put in place a treatment to remove them totally or partially. According to the provisions of Article 4, these treatments have to be authorised: those limited to filtration or decanting, possibly preceded by oxygenation (covered by Article 4 a) can be authorised at national level while other treatments have to be assessed by the European Food Safety Authority (EFSA) and approved at E.C. level according to the E.C. relevant procedure (Article 4.1 b and c).

# II) SCOPE AND PURPOSE OF THE E.U. ASSESSMENT.

## II.1. Scope of the E.U. assessment.

NMW treatments need firstly to be safe and secondly to comply with additional legal requirements related to quality criteria.

In order to meet E.C. requirements, the treatments liable to be used to remove specific constituents shall:

a) be justified with respect to the water composition;
b) not alter the composition of natural mineral waters as regards the essential constituents which give them their properties;
c) only apply to the removal of constituents naturally present in water and not be the result of potential chemical or microbiological contamination of the spring;
d) not induce the formation of treatment residues at a level liable to represent a risk for public health.

The food safety assessment is the sole competency of EFSA. Other qualitative and technological criteria need also to be assessed to determine the eligibility for NMW treatment but are outside the scope of EFSA assessment.

At the Standing Committee of the Food Chain and Animal and Plant Health of 23rd June 2005, it was agreed by the Commission and the Member States that the technological assessment will be performed by an ad hoc expert working group. This working group is composed of experts who have been selected by the Member States competent Authorities.

## II.2. Purpose of the technological assessment.

The purpose of the technological assessment is to evaluate the manganese and the iron oxihydroxide processes for the removal of manganese and arsenic with respect to the qualitative and technological aspects mentioned above.

The report on the E.U. technological assessment is intended for:
- The EFSA as a contribution for its own assessment.
- The Commission and the Member States for further consideration in view of the E.U. authorisation of the treatment.

This report has been established on the basis of the dossiers **(list in Annex I)** forwarded to the Commission by the industry, national food safety agencies and specialised laboratories in water treatment.

The data provided in the annexes have been chosen among a large panel of results from industry. They are representative of variety of types of water and of media used by NMW industry.

# III) BACKGROUND

## III.1. Screening of available treatments for drinking water treatment

Current drinking water treatments for arsenic and manganese removal include:
- Decarbonation with limestone .
- Membrane filtration: nanofiltration, reverse osmosis and electrodialysis of arsenic (+V).
- Coagulation / flocculation/– decanting / filtration
- Coagulation on a filter with iron salts:

None of these treatments currently used for drinking water treatment can be applied to natural mineral waters as they modify the mineralization content of the water.

## III.2. Screening of eligible treatments for NMW treatment.

### III.2.1. Oxidation processes.

The oxidation may be produced by $O_2$ from compressed air or by ozone.

#### III.2.1.1 Removal of arsenic by siliceous sand filters.

- In the presence of iron.

When dissolved iron is present, arsenic -as arseniate (As V) - is eliminated by adsorption on iron hydroxide produced by oxidation according to the formula:
$3\ H_2AsO_4^- + Fe(OH)_3 \rightarrow\ Fe(H_2AsO_4)_3 + 3\ OH^-$

This mechanism has often been observed on deferrisation layers by oxidation and filtration. Total elimination of the arsenic can be achieved on this layer even in the case of extremely high concentrations of iron provided a high level of oxidation is applied.

Co-precipitation of As (+V) is possible in the event of treatment of iron and manganese (with prior oxidation with ozone). These are the As (+V) arseniates which are the best adsorbed: elimination of arsenic therefore requires prior oxidation ($O_3$) to change from the As (+III) state to the As (+V) state since oxygen (O2) oxidises arsenic (+III) at pH 7.5 only very slowly.

- In the absence of iron.

The above treatments can't remove arsenic when iron is lacking.

#### III.2.1.2 Removal of manganese by siliceous sand filters.

- In the presence of iron.

Iron and manganese dissolved in NMW can be removed by classical oxidation by compressed air only when the redox potential is not too low and the pH higher than 7 for manganese removal.

Like iron, manganese can be oxidised by dissolved oxygen in water to form an insoluble precipitate, which can be removed by filtration. However, unlike iron, the oxidation rate is much slower.

- In the absence of iron.

When dissolved manganese is present in the water, a natural coating of the surface of sand grains can naturally occur: this coating may lead to the removal of manganese, even in the absence of iron.

The mechanism is then the same that those described in chapter V.1 and V 2.

The process only becomes truly efficient after a period of "maturing" (extending from several days to several weeks) of the filter(s). During this period, "coating" of the grains of siliceous sand occurs by the manganese oxides.

It has been observed that the presence of this deposit of solid manganese oxide can be used to reduce, or even suspend, recourse to a chemical oxidant and that oxidation by dissolved oxygen is efficient. After this maturation, the filter bed acquires an adsorption and a catalytic activity that is similar to that of manganiferous sand. The coating of $MnO_2$ on siliceous sands can also provide for the removal of some arsenic.

To increase the rate of oxidation and to facilitate removal in water treatment, strong oxidants (ozone) can be added. Removal of manganese and iron can be obtained by action of dissolved ozone and arsenic is co-removed

### III.2.2. Treatments with manganese and iron oxihydroxides.

These treatments are those which are assessed in this report.

## IV) GENERAL PRINCIPLES OF MANGANESE AND IRON OXIHYDROXIDE TREATMENTS BASED ON SELECTIVE ADSORPTION

Natural manganiferous sands have been used since the twenties to retain certain elements such as manganese in waters used for public supply.

There are two generic types of media used for natural mineral water treatment: the manganese oxihydroxides and the iron oxihydroxides. They are summarised in Table 1 below.

Table 1 Summary of media types and mechanisms of action

| Media type | Origin | Mechanism of action |
|---|---|---|
| Manganese oxihydroxides | Natural or synthetic | Adsorption and catalytic oxidation |
| Iron oxihydroxides | Natural | Adsorption and catalytic oxidation |
| Iron oxihydroxides | Synthetic | Adsorption (for Akaganeite)<br>Adsorption and catalytic oxidation (for others) |

# V) ACTION MECHANISM

The process consists of retaining undesirable elements of natural mineral waters on manganese or iron oxihydroxides, natural or synthetic materials with a large specific surface area.
For both media, the process combines two phenomena:

- a physico-chemical adsorption on the media surface,
- a catalytic oxidation of adsorbed elements involving the oxygen dissolved in the water.

Iron, manganese and arsenic which are naturally present in water in reduced form can be retained on these media by selective adsorption and then be oxidised. The oxidation occurs much more slowly than the adsorption, but is important because it creates a larger variety of adsorption sites.

## V.1. Selective adsorption on surface sites

The selective adsorption comes from the hydroxyl groups situated on the surface of the grains of manganese or iron oxihydroxides in aqueous medium. It is a rapid mechanism, which creates new adsorption sites.

The removal of arsenic or/and manganese by a metal based media (containing Mn, Fe) involves the following principles:

- The hydrated sites of the surface, depending of the pH, react like acid or base.
This give new charged sites:
positively charged: $\equiv \text{S-OH}_2^+ \leftrightarrow \equiv \text{S-OH} + \text{H}^+$
or negatively charged: $\equiv \text{S-OH} \leftrightarrow \equiv \text{S-O}^- + \text{H}^+$
Where S can be the metal of the media: Fe, Mn.

- These new charged surface sites and the pre existing sites are acting in the adsorption of the dissolved ions in the water. They can adsorb the cations (such as manganese) or the anions (such as arsenates, arsenites and fluoride) dissolved in the water, depending of the pH and the charge of the sites.
For cations (M): $\equiv \text{S-OH} + \text{M}^{2+} \rightarrow \equiv \text{S-OM}^+ + \text{H}^+$
For anions (A): $\equiv \text{S-OH} + \text{A}^{2-} \rightarrow \equiv \text{S-A}^- + \text{OH}^-$
Where M are dissolved cations and A are dissolved anions in water.

The above mechanisms may give different types of sites after the adsorption phase depending on the pH of the reaction.

## V.2. Catalytic oxidation of adsorbed ions

- Manganese is often present in natural mineral waters in the least oxidised, relatively soluble form $Mn^{2+}$. Its stability depends on the pH, the dissolved oxygen and the presence of complexing agents.

- Arsenic (As) is naturally present in natural mineral waters as complexes at two oxidation stages: arsenites [As (+III)] and arsenates [As (+V)], both adsorbed on media.
When As (III) is present, it is catalytically oxidised to As (V) after adsorption. Generally this step is not necessary as arsenic is usually present as As (V).

The adsorbed ions are submitted to a slow catalytic oxidation from the media. The catalytic oxidation of $Mn^{2+}$ into $Mn^{4+}$ is an indirect oxidation of already adsorbed ions on the media in a similar mechanism as described in Annex II for regeneration.

It differs from the direct oxidation of ions dissolved in the water when using oxidants such as oxygen, ozone etc…because it is an oxidation of an adsorbed ion. Catalytic oxidation is a very slow mechanism versus adsorption.

## V.3. Affinity and selectivity

The affinity is the ratio of adsorbed ions versus the quantity of the same ions dissolved in the initial water to be treated. This affinity depends of the absorbing minerals composing the media and the process conditions including the pH.

The affinity of the most common metal oxides for metals under common pH range (6 to 8) is often as follows:

For manganese oxihydroxide:
For cations: Pb > Hg = Cu > Zn > Cd > Co > Mn
For anions: $OH^- > H_2AsO_4^- > H_2PO_4^{2-} > H_2SiO_4^- > F^-$

For iron oxihydroxide:
For cations: Pb > Hg = Cu > Zn = Fe > Cd > Co = Ni > Mn
For anions: $OH^- > H_2AsO_4^- > H_2PO_4^{2-} > H_2SiO_4^- > F^-$

The selectivity is the performance of the process to remove specific ions from the treated the water. The selectivity depends on the choice of the mineral composition of the media and on the process conditions.

## V.4. Co-removal of other undesirable elements

The media allow the adsorption of other cations and/or anions which are dissolved in the water such as fluoride, nickel, cadmium, uranium, copper, zinc, cobalt, mercury, lead , barium etc… They are also undesirable constituents which are naturally present and do not result from any contamination of the source. They are usually designated as trace elements.

The treatment process may lead to the simultaneous removal (co-removal) of these trace elements under the same operating conditions as for iron, manganese or arsenic removal.
In the case of drinking water treatment, the lists of the trace elements which are likely to be removed with manganese and iron oxihydroxide media are presented in annex III.

## VI) MEDIA DESCRIPTION

Media based on oxihydroxide of manganese or iron are currently used for drinking water treatment. They are characterised by a great diversity of nature, mode of production or preparation, and composition. Nevertheless, their mode of action is common.
An overview of the different media available is presented in annex IV.

### VI.1. Screening of media

For practical use the media can be classified according to their mode of production: they can be either naturally occurring or synthetic:

- The natural materials are ores composed essentially of the oxihydroxide minerals or are granular materials (sands) coated with oxihydroxides.

- Synthetic coated media are also available and produced by chemical treatment of granular material.

- Recently, proprietary synthetic iron-based media have been developed specifically for removal of arsenic. Among them, the synthetic media Akaganeite operates only by adsorption, and do not provide any catalytic oxidation of adsorbed elements.

### VI.1.1. Media based on manganese oxihydroxides

These media are usually designated by the name “manganiferous sands”.

- **Natural mineral ores**

Natural mineral ores are rocks containing a significant part of manganese oxihydroxides and which may be used for water treatment. They have been prepared, concentrated, ground down and sieved to provide a defined granulometry. They also include other minerals such as iron oxihydroxides, silica, aluminium, chromium, vanadium…
Among the natural ores, common varieties are mixing of pyrolusite, todorokite, birnesite... These ore minerals are selected mainly for their composition to achieve the desired selectivity and therefore their performance.

- **Natural coated materials**

Sands coated with a layer of oxihydroxide are naturally available and only need cleaning and grading to produce media for water treatment.
Coated material can also be produced during water treatment. This "auto generation" may occur naturally in some situations as water passes through the media bed. For treatment of public water supplies, this coating mechanism is usually accelerated by adding oxidant, typically chlorine or potassium permanganate, to the water being treated.

- **Synthetic materials**

It is sand coated with oxihydroxide of manganese, which is produced by treating natural glauconite sand or sand with manganese sulphate followed by potassium permanganate, so that a film of manganese dioxide covers the surface of the grains.
It is sometimes referred as “green manganised sand” or "green sand".
Synthetic materials may also be composed entirely of oxihydroxide of iron or manganese produced by chemical way, for example potassium birnessite.

For all media a check of the composition and of the stability is necessary prior to their use. This is especially important because the media is generally composed of different oxihydroxide minerals (annex IV). The properties of the media result directly from the characteristics of the different minerals composing the media.

### VI.1.2. Media based on iron oxihydroxides

The same categories exist for iron oxihydroxides, except the synthetic coated materials.
The main media types currently used for arsenic removal from drinking water are the granular iron oxihydroxides, which could be used in different mineralogical forms. One of the most efficient synthetic mineral in removing arsenic from water is the β form named Akaganeite : β FeO. (OH, Cl).

## VI.2. Solubility of the media throughout the process

The solubility of the media must be examined to avoid the release of impurities during the process but also to guarantee the efficacy of the initialisation and the regeneration of the media.
For each mineral of the media, the solubility of the various minerals in water according to the pH has been studied (annex V).
The choice of the pH and the area of minimum solubility during the process can avoid the release of the media and of the impurities it could contain.

## VI.3. Standardisation of the media

Natural and synthetic filter materials both exist on the market. Due to their geological formation and country-specific characteristics, the natural filter materials have different compositions. Therefore, it is indispensable that the respective filter material is examined with regard to its main, auxiliary and trace elements.

For drinking water treatment, several European standards have been developed, setting up minimum requirements (annex VI). They may be gathered in 2 categories:

- First category concerns definitions (EN 12901) and test methods (EN 12902) to measure migration of impurities from media - so called "***leaching test***" - which must provide information on which of the trace elements bound in the filter material migrate and to which extent.

The test serves as risk analysis prior to the actual implementation. Since the leaching tests must be carried out with a specific synthetic water in accordance with EN standards, the respective filter material must be tested in advance for suitability for the specific mineral or spring water in pilot installations.

- Second category of EN standards relates to the specifications of the different media used:

  - Manganese dioxide (EN 13752),
  - Manganese dioxide coated on limestone (EN 14368*)*,
  - Iron-coated granular activated alumina (EN 14369),
  - Iron (III) hydroxide oxide (EN 15029),
  - Manganese green sand (EN 12911).

These EN standards specify numerous physical, chemical and specific properties (such as respectively particle size distribution, density and surface area…). Among these, some standards (EN 15029 and EN 12911) set up purity criteria about heavy metals while the others (older) - do not set up any but draw the attention of the users to the problem of the leaching of the impurities contained in its supports.

**For NMW treatment, it is therefore necessary, for all media, to carry out leaching tests and performance tests at pilot scale before full scale production.**

Examinations have shown that, depending on the origin of the material and the cleaning or enrichment of the materials, the media composition can be very different: typical values for media produced from natural ores given in the EN standard 13752 ranges from 52% to 78% $MnO_2$. In practice this range is wider than these examples (other concentrations of the ore or synthetic material).

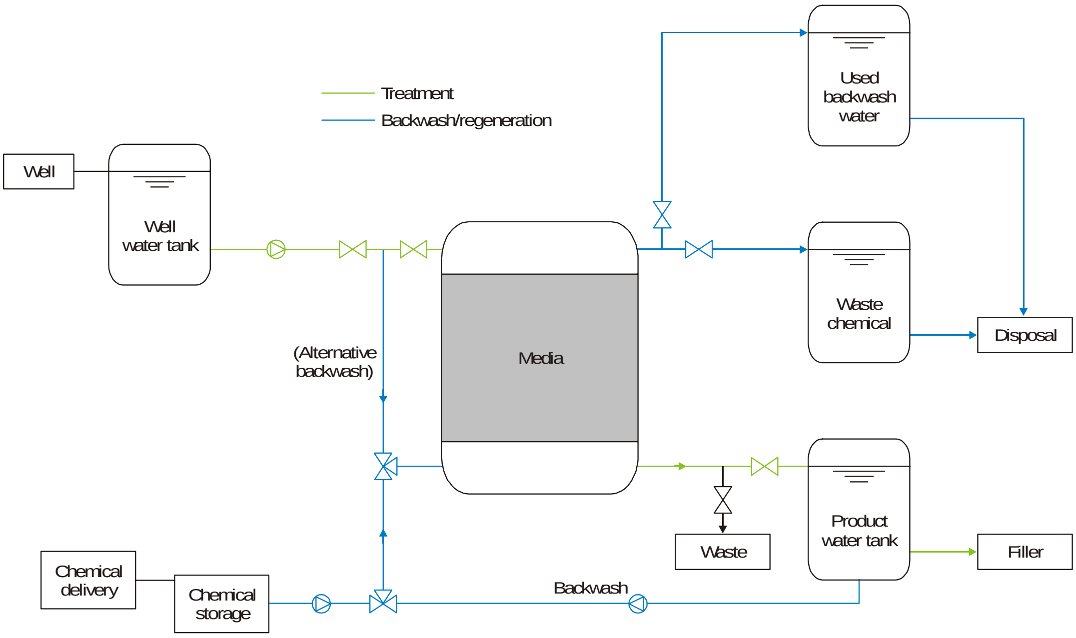
## VII) PROCESS PRINCIPLES

### VII.1. Global treatment schemes

### VII.1.1 Manganese oxihydroxide media

The media are used in conventional filter shells, operating in downflow at typical rates of 10-20 m/h (meter per hour) with 1 m deep beds. Backwashing of the bed is carried out periodically, typically weekly. Some of the accumulated $MnO_2$ on the sand surfaces may be removed by backwashing of the filter, but much of the material remains on the sand, increasing the sand particle size over time.

A general treatment schematic is shown below.



Breakthrough of manganese (or arsenic) is seen for some types of media and modes of operation, with progressive increase in manganese (or arsenic) concentration in the treated water over time. Chemical regeneration of the media is then needed, typically at intervals defined by pilot installation

The media bed can also act as a physical filter, for example to remove iron after aeration of the water. The accumulated iron is removed by backwashing.

### VII.1.2 Iron oxihydroxide media

Treatment using iron oxihydroxide media involves conventional adsorbers, usually operating downflow with the facility to backwash. The schematic is therefore similar to that shown above for manganese media except for the regeneration process which is not commonly used when using Akaganeite. In this case, the media would be disposed of when exhausted.

## VII.2. Integration with other treatments

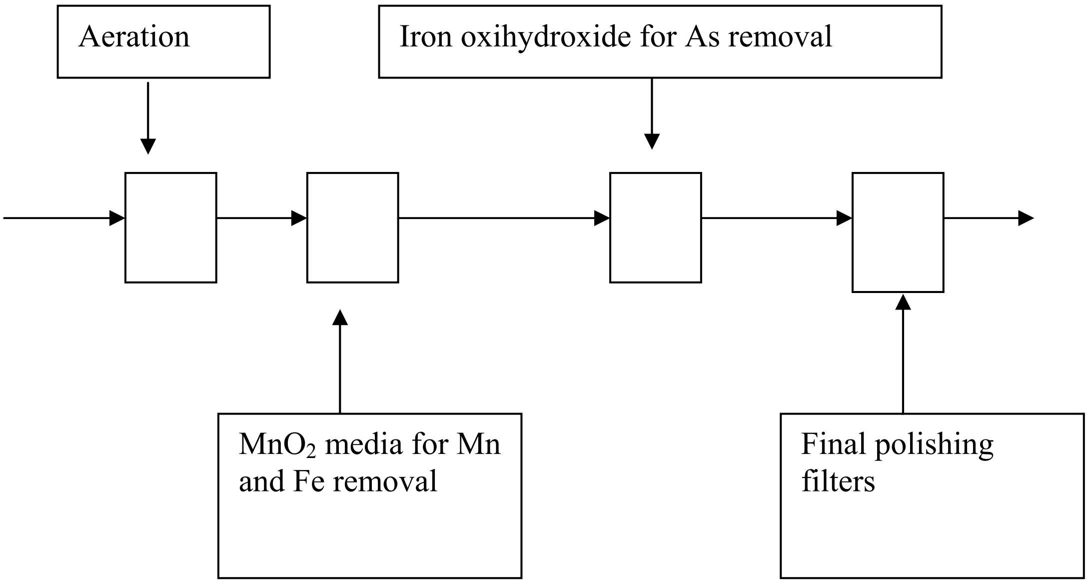
The treatment of arsenic or manganese removal can be combined with other treatments to remove the excess of iron or manganese before the As treatment.

For example, if iron and manganese removal is needed, this would be carried out using aeration and iron removal prior to manganese and arsenic removal. Some removal of arsenic would be achieved by the $MnO_2$ media, increasing the capacity of the iron oxihydroxide.

If fluoride removal was needed, it could be beneficial to use activated alumina to remove both fluoride and arsenic, rather than the iron oxihydroxide media, depending on the related concentrations of each.

An example of a process stream for removal of iron, manganese and arsenic is shown below. This is given for illustrative purposes only, as process selection and optimisation for particular situations need to be considered on a site-specific basis.

**Example of intensive process stream incorporating removal of arsenic, iron and manganese.**



## VII.3. Doping and capture media

The media used are generally a mixture of different oxihydroxide minerals. The so-called "doping" and "capture" media are media where the major oxihydroxide minerals are doping or capture minerals, as described below.

### VII.3. 1. Doping minerals

The solubilisation of the minerals of the filter media releases iron and/or manganese that will re-precipitate in the lower parts of the filter to produce amorphous oxides or oxihydroxides. This lower part behaves in exactly the same way as the sand filters used with iron- and manganese-rich waters. These media are known as doping media for which the material dissolves slowly. Adsorption will cease when the quantity of medium is insufficient and no longer makes sufficient iron and/or manganese available.

To ensure a reprecipitation of Mn lower in the filter, when using doping minerals, the length of the filter or the filtration velocity has to be adapted. Then even for very low concentrations of Mn in the mineral water, the reprecipitation of Mn in the filter takes place.

In the case of a water with low initial content of Mn and low pH (annex VII) , manganese reprecipitates lower in the filter after being dissolved from the doping minerals.
This example illustrates the particular benefit of doping mineral to remove manganese and/or iron when their respective initial concentrations are low.

### VII.3. 2. Capture minerals

A "capture mineral" is one which only adsorbs the ions until exhaustion of its adsorbing capacity without significant dissolution or auto regeneration of the media. The typical one is Akaganeite.
In the case of capture minerals the stability of the media results from their low solubility. There is a direct capture by the minerals of the filter media of the element(s) to be removed: these media are known as capture or adsorbent media: the saturation of the material is reached when all of the adsorption sites are occupied by the specific element to be retained or that can be retained.

## VIII) INITIALISATION AND REGENERATION OF THE MEDIA

Initialisation and regeneration have the common objective to remove the substances which block the adsorption sites.

### VIII.1. Initialisation

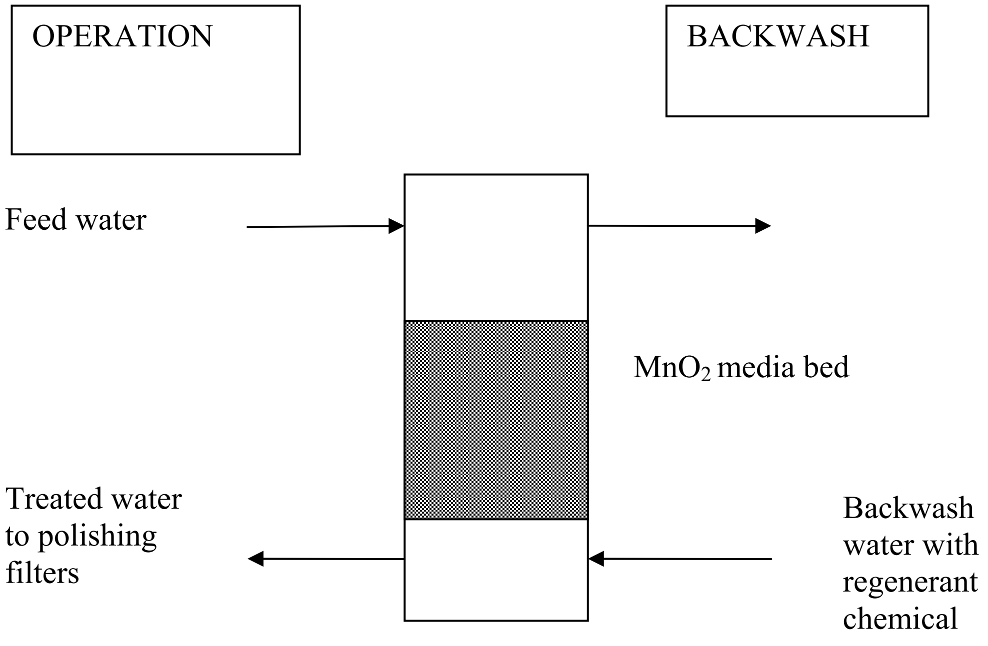
Before use, most of the media need an initialisation process to activate the adsorption sites and to remove the impurities. It is based on a chemical treatment followed by rinsing with water.

### VIII.2. Regeneration

The removal of undesirable elements decreases with time and their concentration in the treated water increases, following a breakthrough curve (as illustrated in Annex VIII), which triggers off the regeneration process.

Regeneration is the chemical process intended to remove the adsorbed ions from the active sites in the acid base regeneration or to create new active sites in the oxidative regeneration.

**Regeneration scheme**



The regeneration process involves passing the regenerant chemical solution through the bed with the filter out of service. This is often done in the opposite direction of the treated flow to maximise the efficiency.
These treatments are always followed by a step of rinsing so that the media does not have any influence on the composition of treated water.

### VIII.2. 1. Manganese oxihydroxide media

Regeneration process could be achieved as below by either:

- a two step treatment using bases (sodium hydroxide) followed by a neutralisation by acid (sulphuric or hydrochloric acid) or,
- an oxidation treatment using potassium permanganate, hypochlorite, chlorine dioxide, ozone, peroxide…(Annex II)

**The base + acid regeneration process is effective for all conditions.** However, depending of the content of Mn, As and Fe in natural mineral waters, other regeneration processes may be used as shown in the following table.

| **NMW composition** | **Alternative regeneration processes** | **remarks** |
|---|---|---|
| Mn alone | Oxidation | |
| Mn + Fe | Oxidation or acid + oxidation | For high Fe concentration, possibility of formation of Iron oxihydroxide precipitate |
| Mn + traces As | Oxidation or acid + oxidation | |
| Mn + Fe + traces As | Oxidation or acid + oxidation | For high Fe concentration, possibility of formation of Iron oxihydroxide precipitate |
| As alone | Only base + acid | |
| As + Fe<br>As + Fe + traces Mn | Only base + acid<br>Oxidation or acid + oxidation | For high Fe concentration: Adsorption of As on the Iron precipitate,<br>For Fe co removal, As is adsorbed on Mn media |
| As + Mn + traces Fe | Oxidation or acid + oxidation | Adsorption on Mn media |

The base/acid regeneration is essentially desorption of the adsorption sites of the media with some dissolution of the media. The oxidative regeneration is essentially the creation of some new active sites. Mechanism of regeneration with oxidant is detailed in Annex II.

The frequency of regeneration may vary according to several criteria: the initial concentration of the undesirable elements, type of media, the kind of interactions, the composition, pH and Eh of the water.

### VIII.2. 2. Iron oxihydroxide media

Options for regenerating this media are listed in the table below.

| NMW composition | Regeneration process | remarks |
|---|---|---|
| As alone | base + acid or no regeneration | Often no regeneration for Akaganeite |
| As + Fe<br>As + Fe + traces Mn | base + acid or no regeneration | |
| As + Mn + traces Fe | base + acid or no regeneration | Adsorption on neoformed Mn media |

For the removal of all above elements these media could be regenerated. But it can be chosen not to regenerate the media if the disposal of solid waste with high arsenic content is more acceptable than disposal of liquid waste arising from regeneration.

### VIII.3. Types of chemical solutions used for regeneration

For safety and efficiency, the media, regeneration chemicals and materials used in the process should comply with the E.U. or national standards for drinking water treatment.

## IX) PROCESS PERFORMANCE AND OPTIMIZATION

### IX.1. Impact of initial manganese and arsenic contents

High level of manganese above 2000 µg/l and arsenic above 500 µg/l may be found for some NMW. Efficiency of the treatment depends on the composition of the water (competing ions for adsorption sites) and the nature of the media (kind and number of adsorption sites).
Experience shows that these waters can be treated to achieve concentration below10 µg/l for manganese and below 5 µg/l for arsenic.
If necessary these levels can be achieve after several stages of treatment with this media.
For any composition of raw water, the EU NMW maximum limits for manganese (500 µg/l) and arsenic (10 µg/l) can be achieved.

### IX.2. Impact of pH

### IX.2.1. On arsenic and manganese removal.

- Arsenic removal.

On account of the high affinity of this media for $OH^-$ ions, adsorption of arsenic is much more effective at an acid pH (in a pH-range of 6 to 6.4) than at an alkaline pH.

However, experience of the treatment of drinking water has shown that the media can still be used to remove arsenic as long as the pH is not higher than 8. For NMW with high pH, the permitted addition of $CO_2$ can be used to lower the pH.

Not all mineral waters can be treated using $CO_2$ in the natural area of the treatment due to the very varying mineralisation, as this can lead to a disturbance of the lime-carbon dioxide balance.

Precipitation of calcium carbonate can occur, which can lead to changes to the characteristic composition. The treatment used must therefore be optimally adapted to the relevant mineral water type.

- Manganese removal.

On account of the high affinity of this media for $H^+$ ions, adsorption of iron, manganese and other cations is much more effective at an alkaline pH (in a pH-range of 7 to 9).

### IX.2.2. On other substances removal

The relative removal of undesirable substances other than arsenic, manganese and iron will also depend on the pH of the treated water. When the pH is slightly alkaline, interference from certain cations is observed. This may cause competition for the adsorption sites, and therefore a decrease in the manganese and arsenic adsorption capacities.

### IX 2.3 On iron and manganese release.

Reducing the pH improves the arsenic removal on both manganese and iron oxihydroxide media but increases the risk of iron and manganese release from the media and decreases removal performance for iron and manganese from the water.

### IX.3. Impact of the aging of the media

The aging of the media, for all types of oxihydroxides, has an impact on its composition and properties (adsorption, dissolution). This results from an evolution to the stable mineral form. For example, the following changes are observed:

amorphous $Fe(OH)_3$ → ferrihydrite → goethite.
amorphous $MnO_2$ → turbostatic birnesite → birnesite.

The duration and the condition of storage prior to use could reduce the adsorption capacity of the media. The aging effect of the media during operation is slower because of the regeneration.

## X) IMPACT ON NMW CHARACTERISTIC COMPOSITION

### X.1. Legal requirements

The media used should not cause any changes in the treated NMW except for the removed elements. In particular, the characteristic composition of the NMW, within the natural fluctuation margin, should not be changed.

### X.2. Impact on the characteristic composition

The impact of arsenic and manganese removal on the composition -including some trace elements- has been studied on various NMW using both manganese oxihydroxide or iron oxihydroxide media.

### X.2.1. Manganese oxihydroxide media

Treatment has been applied on various NMW to remove As and Mn. Results of analyses from both pilot and industrial plants are presented in annex IX-1 for Mn removal (springs A to E) and for Mn and As removal (spring F). Results show that characteristic anions and cations are not modified within the so-called "**natural fluctuations**" for both the iron media and the manganese media.
Co-removal of some trace elements (Ni, Co, Zn) is observed.

### X.2.2. Iron oxihydroxide media

Treatment has been applied to remove arsenic on Akaganeite media for several NMW. The results are presented in annex X-1 for Na-HCO3 NMW, (total salt dissolved = 667 mg/l), annex X-2 for Ca-HCO3 NMW (a sparkling NMW of total salt dissolved of 660 mg/l) in annex X-3 for oligomineral water (total salt dissolved of 110 mg/l) in and in annex X-4 for high mineralized water (total salt dissolved of 1680 mg/l). Co-removal of some trace elements (Al, U, Zn, Mo, Cu) is observed (Annex X-5).

In all cases analyses show no modification of the characteristic composition of NMW for both cations and anions. A slight decrease of silica can be observed for alkaline pH (7.5 to 7.8) but be corrected by addition of $CO_2$ as shown in annex IX-2.

For all tested waters, the results show that the observed variations of mineral composition are very low and remain within the limits of the so-called "natural fluctuations". These tests show that NMW with different characteristic compositions, which are treated with both types of media (Mn and Fe), are not affected by the treatment during all the process life.

## XI) IMPACT ON MICROBIOLOGY

### XI.1. Microbiological risks

### XI.1.1. Risk of proliferation of revivable total colony count

The treated natural mineral waters come from sources, which must be protected from microbiological hazards. It may, however, contain bacteria naturally present in water at source. They are called in directive 80/777/EEC "revivable total colony count". Iron or manganese oxihydroxides are porous medium, which like most granular media, may be colonised by bacteria, with the formation of a biofilm.

Results of microbiological analyses show that there is no impact of iron or manganese oxide medium filtration on the microbiological quality of the NMW (Annexes XI-1 and XI-2).
The iron or manganese oxide medium may also adsorb natural organic substances from the water (humic and fulvic acids). However, NMW contain little or no organic matter.
In addition, the adsorption of these organic substances does not constitute a risk of bacterial proliferation, because they do not contain any significant concentrations of biodegradable organic carbon.

### XI.1.2. Risk of colonisation with nitrifying flora

When NMW contains ammonium ions and is previously aerated to eliminate iron or sulphur compounds, for example, nitrification may occur. Nitrification is the biological oxidation of ammonium ions into nitrate (1 mg of ammonium produces 3.4 mg of nitrate). An intermediate in this process is nitrite, which is of greater health concern than nitrate, and can occur as a result of incomplete nitrification.

Nitrification occurs only if the pH of the water is higher than 6.5–7. It does not occur under pH 6.5. If the water remains at this pH (sparkling water), nitrification – even incomplete – does not occur during storage. If the pH is increased to above 6.5, there is a risk that the production of nitrites will occur.

With this media, the use of oxygen is normally not needed, thus minimising the risk from nitrification. This risk is not specific to filtration with iron or manganese oxihydroxide but occurs with all filtration systems. If the water is only partially aerated, the risk of nitrite production would be high: for full nitrification, to avoid nitrites, 4.5 mg of oxygen per mg of ammonium ions is required. If complete, this nitrification process stabilises the water effectively and prevents partial oxidation of ammonium ions into nitrite during storage of the bottled water. In normal running conditions of the process, this risk is negligible.

### XI.1.3. Risk of colonisation with microbial flora which remove iron and manganese

Acid pH conditions promote the colonisation by this bacterial flora, which would provide a beneficial effect in terms of iron and manganese removal.

### XI.1.4. Risk of colonisation with a reducing flora leading to the formation of nitrites and sulphides

Under normal circumstances, when the filter is in operation the dissolved oxygen in the water should be high enough to prevent this phenomenon from occurring. However, when the filter stops, bacterial proliferation can occur with the result that there are large amounts of bacteria in the water as soon as the filter starts working again. In particular, a reduction of nitrate to nitrite and a colonisation with a denitrifying flora can occur, which may continue to produce nitrite when the filter restarts.

These phenomena depend on the:

- Quality of the water and in particular the amount of organic carbon adsorbed by the media;
- Temperature of the water in the filters when stopped (this temperature may be quite different from that of the water during operation);
- Length of stoppage.

In the case of sulphated water, sulphides might be produced through sulphate reduction. After a prolonged stoppage of an adsorber (around 24 hours or more), it is therefore essential to restart it only after a regeneration and/or disinfection stage. One solution is to always circulate water in a closed circuit in the filter with slight aeration, thereby avoiding stagnation of water. With regard to NMW treatment operating conditions, the limited size of the filters and aeration conditions normally prevent this risk.

## XI.2. Impact of regeneration on microbiological growth

The regeneration stage has a great importance from the microbiological point of view. The regenerant solutions all have a bactericidal effect. The biofilms are destroyed and then eliminated by the rinsing step.
When some media based on iron oxihydroxide are used without regeneration (Akaganeite for example), an abnormal development of microbial flora can occur and the disinfection of the media would be necessary.

## XI.3. Methods of disinfection of the media

### XI.3.1 Manganese oxihydroxide media

#### 1) Base-acid treatment.

Under normal conditions, the base-acid process is sufficient to provide a disinfection of the media. However, it may be necessary to implement disinfection stages of the media separately from regeneration. In the case of accidental contamination or after stoppage of the filter, an additional regeneration cycle will solve the problem.

#### 2) Hot water or steam treatment.

Hot water above 85°C or steam will provide effective disinfection. At this temperature, the biofilm is destroyed and then eliminated by rinsing.
This would be the recommended disinfection method when the base-acid regeneration treatment is not available, provided that this is compatible with media mechanical resistance.

### 3) Oxidative treatments.

Oxidative treatments such as hypochlorite, permanganate, ozone… used for regeneration are rarely used for disinfection. These treatments may form by-products when organic matter is present on the media (see chapter XII. 3) and need special consideration.

### XI.3.2 Iron oxihydroxide media

### 1) Base-acid treatment.

When the media is regenerated using base-acid solution, this will provide effective disinfection. In case of an accidental microbiological contamination, the regeneration process can then be implemented.

### 2) Hot water or steam treatment.

Hot water above 85°C or steam will provide effective disinfection. At this temperature, the biofilm is destroyed and then eliminated by rinsing.
For some media (for example synthetic Akaganeite) steam treatment may cause partial pulverisation of the media and its migration into the treated water.

### 3) Oxidative treatments.

Oxidative treatments such as hypochlorite, permanganate, ozone…may be used for disinfection. However, these treatments may form by-products when organic matter is present on the media, especially if there is no regeneration process.
It will be necessary to carefully rinse the media and apply very effective control procedures.

## XII) RESIDUES

### XII.1. Substances present in the media

For manganese oxihydroxide media (natural mineral ores) and iron oxihydroxide media, extensive analyses were carried out concerning four typically used materials to check for impurities in the media and their release in water.

### - Composition and impurities of the media

The media may contain impurities in very low concentrations (annexes XII-1 for iron oxihydroxides and annexes XII-2 to XII-5 for manganese oxihydroxides). They should not leach into the treated water. However, there are standards and test procedures available (leaching test EN 12901 and 12902) for all media for public drinking water treatment.

### - Impurities released during leaching tests

The standards for leaching tests should be used as the basis for selection of media for natural mineral water treatment. Results of leaching tests on synthetic water according to above standards are presented in Annexes XIII-1 for Fe and XIII-2 and XIII-3 for Mn.

For synthetically produced iron oxihydroxides, only low levels of trace compounds are found in the media composition (Annex XII-1). Nevertheless, a leaching test was conducted with this material and remains necessary before the use of this type of media (Annex XIII-1). It shows that very small quantities of trace elements migrate into the solution; however, the impact of this can be minimized by starting operation with initialisation and a sufficient period of rinsing.

**- Impurities released in the treated water during operation (pilot testing)**

Operational tests were carried out with both drinking water and natural mineral water at pH 6.0 and 6.5 to fit with the variations of pH which are encountered in practice with NMW to be treated

For manganese oxihydroxides media (media compositions described in annexes XII-2 and XII-3), **the results of water analyses before and after treatment show that no impurities are released during the treatment** (annexes XIV-1 to XIV-8).

### XII.2. Reaction products (by-products) with the media

Various mechanisms occur inside the media: adsorption, catalytic oxidation, dissolution, migration, reprecipitation for iron and manganese oxihydroxides.

The only significant mechanism in relation to by-products is oxidation.
The studies of the evolution of the redox potential during the process for 5 different waters show that redox potential necessary for adsorption and catalytic oxidation lies between 200 to 400 mV (lower than the 600 mV obtained by the use of air with ozone).

Therefore, this very low oxidation action (due to low redox potential), combined with the very low organic content in NMW, exclude the formation of by-products, as shown in Annexe XV-1 for manganese oxihydroxide media and Annex XV-2 for iron oxihydroxide media).

These results are confirmed by more detailed water analyses before and after treatment provided in Annex XVI-I (iron oxide) and Annex XVI-2 (manganese oxide with oxidising regeneration).

### XII.3.Reaction products with chemicals used for initialization, regeneration and disinfection

- **With base-acid treatment**

The chemicals used for initialisation and regeneration clean the media by desorbing the adsorbed ions and dissolving the external surface of the media. There is no oxidation effect and therefore the treatment does not create by-products by reaction with media constituents.

- **With an oxidant**

Various chemical oxidants are sometime used for initialisation, regeneration and disinfection: chlorine, chlorine dioxide, potassium permanganate, peroxides, ozone…

**Chlorination treatments, used for sand filters, may pose a particular problem in this case.** Natural organic substances adsorbed on the media, comprising humic or fulvic acids, are the main precursors for by-products from reaction with chlorine in water treatment: trihalomethane, halogen derivatives of acetic acid or acetonitrile. **Chlorination cannot therefore be recommended for disinfection of the media in this case.**

In case of use of oxidants, it will be necessary to carefully rinse the media and apply very effective control procedures. Results after disinfection with ozone and appropriate rinsing have shown no by products formation (Annex XVII).

## XIII) MONITORING AND CONTROL

### XIII. 1 MONITORING

The arsenic and/or manganese content of the final product need to be measured periodically in order to ensure that there is an efficient removal of these undesirable constituents.

The final product is also to be analysed at regular intervals as to its essential and characteristic constituents, in order to ensure that the composition of the natural mineral water remains within the margins of naturally occurring fluctuations. The determination of the main and trace components should therefore be checked at regular intervals.

### XIII. 2 CONTROL

A process protection has to be documented by a risk analysis and an HACCP system should be implemented as required by the E.U. legislation. An example of HACCP application is presented in **Annex XVIII**.

## XIV) CONCLUSION

The following conclusions can be established:

- The manganese oxihydroxide and iron oxihydroxide media provide for **an efficient process for the removal of manganese, iron and arsenic from** NMW, even with high initial concentrations, if appropriate media and operating conditions are used; they can be adapted to many different situations and have in many cases avoided the use of ozone-enriched air.

- The simultaneous co-removal of other undesirable trace elements is also achieved within the same operation.

- For each natural mineral water and each filter media pilot tests should be implemented at sufficient scale to check the efficiency and the selectivity of the process, and the absence of release of impurities from the media.

- Operating conditions, composition of the media and pH conditions should be optimised according to each NMW characteristics, to achieve effective and selective iron, manganese and arsenic removal.

- The treatment **does not cause any significant change of the characteristic composition** of NMW when appropriate operating conditions are maintained.

- Both for efficiency purpose and for avoiding release of substances into the water, manganese oxihydroxide and iron oxihydroxide media, chemical reagents and materials used should **comply with the European standards** and, where necessary, national standards applicable to drinking water treatment;

- There is no evidence of significant release of impurities, provided an appropriate selection of the media used (included pilot testing) and an initialisation process is applied and good operating conditions are maintained;

- Depending on the NMW composition, **the pH could be adapted with $CO_2$ to focus on manganese and/or arsenic removal**, provided it does not cause an impairment of the treated water quality. However the risk of iron and manganese release when reducing the pH of the treated water shall be monitored;

- According to available results of analyses, there is **no production of organic and inorganic by-products**.

- The microbiological analyses available **do not show any risk of microbiological contamination**, provided good operating conditions are applied.

# ANNEX I: LIST OF DOSSIERS FORWARDED TO EFSA

- "Application for permission to use metal oxide processes on natural mineral waters" forwarded by the **Belgian federation of the water and soft drink industry (FIEB / VIWF).**

**- "Update on the elimination of manganese and arsenic from natural mineral waters and spring waters: use of manganiferous sands" forwarded by the French Chambre Syndicale des Eaux Minérales Naturelles.**

- "Evaluation of treatments to remove specific mineral constituents present in natural mineral waters and spring waters- report to water expert committee" forwarded by the **French food safety agency AFSSA.**

- "Evaluation of the use of metal-oxide coated sands for the treatment of water human consumption and natural mineral waters- Metal oxide coated filtration materials- bibliographic study" forwarded by the **French food safety agency AFSSA**.

- "Report on the use of GEH for the selective removal of arsenic from mineral waters" forwarded by the w**orking Group of III Section of Consiglio Superiore della Sanità (CSS) of the Ministero della Salute of Italy.**

- Analytical data (German report) provided by the **SGS INSTITUT FRESENIUS GmbH (Germany) forwarded by German mineral water federation (VDM).**

# ANNEXE II: STUDY OF THE MANGANESE MEDIA REGENERATION BY OXIDATION

## CASE OF Mn REMOVAL

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January 2007

## 1. Introduction

To understand the effect of regeneration on the adsorption sites of the media, we have examined the media before and after regeneration by oxidation with ozone treatment. As the practise of treatment shows a different procedure in the case of manganese removal and in the case of arsenic removal, we decided to study the effects in both cases. This report gives the results of the first case: removal of Mn essentially.

## 2. The original Media

The media -an oxihydroxide of Mn- used for the tests is a concentrated natural ore of Mn. The chemical composition of the media is given in Annex XII-5 and the leaching test in Annex XIII-3 of the working group report.

The XRD (x-ray diffractometry) study of the media gives the mineral composition of the original media. The main minerals are two manganese oxihydroxides: NSUTITE and PYROLUSITE. Both are chain-manganates (ino-manganates). The chain is composed of octaheders in which the corners are occupied by oxygen and the center by $Mn^{+4}$.

These octaheders are also the elementary blocks of all the oxihydroxides of Mn. Therefore the d-spacings with values around 2.40 – 2.45 Å and 1.40 – 1.42 Å are common to many different oxihydroxides of Mn.

Furthermore the particle sizes of the crystallites are often so small that the diffractions lines appear broad and diffuse. The identification of the minor mineral components is thus more difficult as broad peaks can often be attributed to different manganese minerals.

Among the possible minor minerals of the media we find todorokite, pyrochroïte, cryptomelane for the Mn-oxyhydroxides and perhaps a 7 Å silicate. The presence of **quartz** ($SiO_2$) is sure because the lines of this mineral are sharp due to his crystalline state. Compared with the media after water treatment and even after regeneration the crystallites size of the minerals is better in the original media.

## 3. The treated water

The ion balance of the treated mineral water is presented in German report (mineral water – Type 6). The only important difference after treatment is the reduction of manganese from 1300 µg/l to 12 µg/l. A very slight reduction of cesium, cobalt, chrome and nickel is also observed.
We can thus qualify the test as removal of Mn with negligible co-removal of Cs, Co, Cr and Ni.

## 4. The Media after water treatment and before regeneration

After water treatment the media is mainly composed of "turbostratic" birnessite, a very poorly crystalline variety of the mineral birnessite. This variety called "turbostratic" birnessite was discovered in the deep-sea manganese nodules. In the study of those nodules (GLASBY, 1977) a simplified structure of this mineral describes it as layers of $MnO_2$ (octahedra) separated by adsorbed $Mn(OH)_2.2H_2O$ and by $H_2O$.

Recent studies of synthetic material confirm this structure and the possible absorption of other ions between the layers of $MnO_2$. The dehydratation and oxidation of the absorbed $Mn(OH)_2.2H_2O$ to new $MnO_2$ has been already cited in the deep-sea nodules.

This oxidation of the inter-layer adsorbed $Mn(OH)_2.2H_2O$ can be followed in XRD by the structure change from the 2 lines-birnessite to turbostratic birnessite and then to well cristallised birnessite.

A complete range from nearly amorphous to crystalline birnessite can be recognised by the change in the number and the intensity of the X-ray diffraction lines. This evolution translates the growing crystalline size and a decrease of the disorder in the crystal structure.

In the sample of the media after water-treatment we find by XRD a turbostratic birnessite where the absorbed $Mn(OH)_2.2H_2O$ is dominant in the interlayer. This is confirmed by the enrichment in $Mn^{2+}$, between the original media and the media after water treatment and before regeneration. The media is richer in $Mn^{2+}$ and water content as indicated by infra-red spectroscopy and thermogravimetry. The presence of $Mn(OH)_2$ absorbed in the interlayer is also confirmed in XRD by the line 4,75 Å of pyrochroïte [$Mn(OH)_2$] structure.

## 5. The same media after regeneration

The XRD reveals a composition very similar to the media before regeneration. The main mineral is also turbostratic birnessite, but the cristallinity is better due to oxidation of a part of the absorbed $Mn(OH)_2.H_2O$.
This transformation is limited and forms new $Mn^{+4}(O_x, OH_{2-x})$ tetraheders or $Mn^{+4}$-$(O,OH)_6$ bonded by the edges. Those are new adsorption sites which replace a small part of the sites occupied by $Mn^{+2}$.

The evolution of the X-ray lines confirms this limited oxidation.

| X-ray line | 7.3 Å | 3.69 Å | 2.13 Å |
|---|---|---|---|
| Before regeneration | 34 | 14 | 0 |
| After regeneration | 66 | 18 | 2 |

There is only one new line (5 lines birnessite) and the lines are still broad lines but the intensity of the two characteristic lines is greater. This evolution is confirmed by IR-spectrometry and thermogravimetry.

The I-R spectrometry indicates that the number of OH groups with hydrogen-bonding is higher in sample 1 (before regeneration) than in sample 2 (after regeneration). The spectrum also shows already better cristallised $MnO_2$ in sample 2. The thermogravimetry also shows a decrease of adsorbed water and a decrease of $Mn^{2+}$ replaced by $Mn^{+4}$.

The regeneration process does not reconstitute the initial composition of the media before water treatment. The mineralogy after regeneration is very different from that of the initial media.

The regeneration is limited to an oxidation of a part of the absorbed $Mn^{+2}$ complex. This kind of regeneration created some new $Mn^{+4}O_2$ octaheders by oxidation of $Mn^{2+}(OH)_2$ absorbed in the interlayer of the turbostratic birnessite formed by water treatment.

## 6. Conclusion

With this type of water treatment (limited to Mn removal), the water treatment modifies the mineralogy of the media. The main compound after treatment is a phyllomanganate which absorbed the $Mn^{+2}$ from the water in his interlayer.

The adsorbed $Mn(OH)_2$ can partially be restored to $MnO_2$ tetraheders by the oxidant regeneration. The study is based on oxidation of the media by ozone treatment. The same mechanism will apply for other oxidants (permanganate of potassium, hypochlorite…).
In the case of Mn removal the process of the regeneration is not aimed to desorption of initial sites but to formation of new sites in the interlayer of the neoformed phyllomanganate.

**The process can be different for the removal of other ions than $Mn^{+2}$, especially for anions as arsenic complexes for example in NMW with low Mn and Fe content.**

# ANNEX III

## Annex III - 1: supports coated with manganese oxihydroxide (for drinking water)

| Cationic groups | |
|---|---|
| **$Fe^{2+}$** | - Same action as iron oxyhydroxides: the iron is adsorbed and then oxidised<br>- Manganese oxides are more effective than iron oxyhydroxides<br>- Production of sludge is reduced<br>- Adsorption is reduced if the pH falls |
| **$Mn^{2+}$** | - Adsorption kinetics are dependent on water pH (80% loss of adsorption between pH 6 and 8) and the amount of $MnO_2$ deposited on the support<br>- Auto-oxidation of $Mn^{2+}$ by $MnO_2$ requires alkaline pH<br>- Oxidation of $Mn^{2+}$ requires either chemical or biological oxidation<br>- Two stages: selective adsorption followed in some cases by oxidation<br>- The adsorbed manganese is rapidly oxidised by chloride at pH up to 6.1<br>- Efficacy does not depend on the amount of $MnO_2$ deposited but above all on the number of exchange sites |
| **$Pb^{2+}$** | - Same action as iron oxyhydroxides<br>- Importance of pH: acid pH greatly reduces adsorption |
| **$Cu^{2+}$**<br>**$Zn^{2+}$**<br>**$Cd^{2+}$**<br>**$Co^{2+}$**<br>**$Ni^{2+}$**<br>**$Hg^{2+}$** | - Same action as iron oxyhydroxides<br>- Manganese oxides are more effective than iron oxyhydroxides and aluminium oxyhydroxides |
| **$UO_2^{2+}$** | - Same action as iron oxyhydroxides |
| **$PuO^{2+}$** | - Identical behaviour to uranium |

| Anionic groups | |
|---|---|
| **As(III)**<br>**As (V)** | - Adsorption capacity of manganese oxides greater than that of iron oxyhydroxides and, for the trivalent form, greater than that of aluminium oxyhydroxides<br>- Adsorption of trivalent arsenic followed by oxidation into pentavalent arsenic<br>- Quality limit in water: 10 µg/L<br>- Retention of tri and pentavalent forms<br>- Important role of pH: alkaline pH (> 8) greatly reduces adsorption<br>- Competition with fluoride and phosphate ions<br>- Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned. |
| **Se (IV)**<br>**Se (VI)** | - Identical to arsenic |
| **Sb (III)** | - Same action as arsenic |

| | |
|---|---|
| **Sb (V)** | - Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned. |
| **Cr (III)**<br>**Cr (VI)** | - At pH between 4 and 7 trivalent chromium is oxidised into hexavalent chromium and the hexavalent chromium is adsorbed selectively onto the manganese oxides |
| **$PO_4^{3-}$** | - Analogous behaviour to arsenic |

## Annex III - 2 : supports coated with iron oxyhydroxides (for drinking water)

| Cationic groups | |
|---|---|
| **$Fe^{2+}$** | - Removal increases with the extent of the iron oxide layer<br>- Production of sludge is reduced<br>- Adsorption is 20 to 25 times greater on a coated sand than on a conventional sand<br>- Adsorbed iron is oxidised on the support, producing very good results<br>- Iron adsorption depends on pH and the concentration of the oxidisation agent<br>- Adsorption is accompanied by release of $H^+$ ions, although if the pH of the water falls the amount of adsorbed or iron also falls<br>- Water alkalinity plays a very major role<br>- The amount of oxygen required are in the region of 2 mg/ml<br>- Adsorption and biological iron removal are produced at the same time and in the support |
| **$Pb^{2+}$** | - Iron oxyhydroxides produce better results than aluminium oxyhydroxides for adsorption<br>- Adsorption depends water pH and falls greatly with an acid pH |
| **$Cu^{2+}$**<br>**$Zn^{2+}$**<br>**$Cd^{2+}$**<br>**$Co^{2+}$**<br>**$Ni^{2+}$**<br>**$Hg^{2+}$** | - Two stage retention: rapid surface adsorption followed by distribution into the oxide particles<br>- Manganese oxides are more effective than iron oxyhydroxides<br>- Iron oxyhydroxides are more effective than aluminium oxyhydroxides |
| **$UO_2^{2+}$** | - The pH must be between 4 and 10<br>- At a pH of less than 4, $H^+$ ions compete and adsorption does not occur.<br>- At pH over 10, uranium is in a form which is not retained and is returned into solution |
| **$PuO^{2+}$** | - Identical adsorption to that of uranium |

| Anionic groups | |
|---|---|
| **As(III)**<br>**As (V)** | - Important role of pH : Adsorption of trivalent or pentavalent arsenic depends on the water pH. If this is close to neutrality both forms are adsorbed simultaneously.<br>- Retention of tri and pentavalent groups<br>- Competition with fluoride and phosphate ions<br>- Greater adsorption capacity than aluminium oxyhydroxides but less than manganese oxides<br>- Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned. |
| **Se (IV)**<br>**Se (VI)** | - Adsorption onto iron oxides of Se (IV) and Se (VI) groups<br>- Important role of pH |

| | |
|---|---|
| | - The system achieves a concentration of 10 µg/L |
| **Sb (III)**<br>**Sb (V)** | - The action is the same as for arsenic, with the same yields |
| **Cr (III)**<br>**Cr (VI)** | - Only selective adsorption allows retention of hexavalent chromium<br>- Iron oxyhydroxides can retain up to 99% of hexavalent chromium<br>- The presence of pentavalent arsenic reduces chromium adsorption. In this case serial adsorbents must be planned |
| **$PO_4^{3-}$** | - Analogous behaviour to that of arsenic |

# ANNEX IV: IRON AND MANGANESE OXIHYDROXIDE MEDIA TYPES

| CATEGORIES | PREPARATION OF MEDIA | FINAL PRODUCT MEDIA | MECHANISM | ELEMENTS REMOVED IN DRINKING WATER | ACTIVATION / REGENERATION | STANDARDS |
|---|---|---|---|---|---|---|
| **IRON COATED**<br>**(AUTOGENERATED)** | No preparation Sand coating in the filter with iron and Mn from NMW | Iron coated sand | adsorption + catalytic oxidation dissolution or migration in filter or precipitation or adsorption | **Cationic group**<br>cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, zinc,<br>**Anionic group**<br>arsenic, selenium, antimony, chromium, phosphates | NO or YES | Leaching test:<br>EN 12 901 and<br>EN 12 902<br>Media:<br>EN 15029 |
| **IRON BASED OXIHYDROXIDE** | Chemical precipitation from iron salt | Particulate ß Fe OOH.Cl<br>iron coated granular alumina | Adsorption | **Cationic group**<br>cadmium, copper, cobalt, iron, lead, mercury, nickel, zinc,<br>**Anionic group**<br>arsenic, selenium, antimony, (fluoride), chromium, phosphates | NO or YES | Leaching test:<br>EN 12 901 and<br>EN 12 902<br>media<br>EN 15029<br>EN 14369 |
| **IRON ORES**<br>**(NATURAL)** | Natural formation and concentration | Particulate iron oxihydroxide | adsorption + catalytic oxidation | **Cationic group**<br>cadmium, copper, cobalt, iron, lead, mercury, nickel, zinc,<br>**Anionic group**<br>arsenic, selenium, antimony, (fluoride), chromium, phosphates | YES | Leaching test:<br>EN 12 901 and<br>EN 12 902<br>Media:<br>EN 15029<br>EN 14369 |

| CATEGORIES | PREPARATION OF MEDIA | FINAL PRODUCT MEDIA | MECHANISM | ELEMENTS REMOVED IN DRINKING WATER | ACTIVATION / REGENERATION | STANDARDS |
|---|---|---|---|---|---|---|
| **$MnO_2$ COATED (AUTO GENERATED)** | No preparation<br>Sand coating in the filter with Mn and iron from NMW | $MnO_2$ coated sand | adsorption + catalytic oxidation<br>dissolution or migration in filter or precipitation or adsorption | **Cationic group**<br>cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, zinc,<br>**Anionic group**<br>arsenic, selenium, antimony, chromium, phosphates | NO or YES | Leaching test: EN 12 901 and EN 12 902 |
| **$MnO_2$ COATED**<br>**(NATURAL)** | self coating | $MnO_2$ coated sand | adsorption + catalytic oxidation<br>dissolution or migration in filter or precipitation or adsorption | **Cationic group**<br>cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, zinc,<br>**Anionic group**<br>arsenic, selenium, antimony, chromium, phosphates | NO or YES | Leaching test: EN 12 901 and EN 12 902<br>Media : EN 12911 |
| **MnO2 COATED**<br>**(SYNTHETIC)** | permanganate and hydrogen peroxide on greensand<br>or silica and anthracite<br>or other particulate media | $MnO_2$ coated sand, $MnO_2$ coated limestone, | adsorption + catalytic oxidation dissolution or migration in filter or precipitation or adsorption | **cationic group**<br>cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, zinc,<br>**anionic group**<br>arsenic, selenium, antimony, chromium, phosphates | YES<br>permanganate and/or chlorine and/or hydrogen peroxide and/or ozone | Leaching test: EN 12 901 and EN 12 902<br>Media: EN 12911<br>EN 14368<br>CHEMICALS - permanganate: EN 12672 |

| CATEGORIES | PREPARATION OF MEDIA | FINAL PRODUCT MEDIA | MECHANISM | ELEMENTS REMOVED IN DRINKING WATER | ACTIVATION / REGENERATION | STANDARDS |
|---|---|---|---|---|---|---|
| **$MnO_2$ ORE**<br>**(NATURAL)** | natural formation and purification | particulate $MnO_2$ | adsorption + catalytic oxidation dissolution or migration in filter or precipitation or adsorption | **cationic group**<br>cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, zinc,<br>**anionic group**<br>arsenic, selenium, antimony, chromium, phosphates | YES<br>permanganate and/or chlorine and/or hydrogen peroxide and/or ozone<br>ALKALI / ACID | Leaching test:<br>EN 12 901 and<br>EN 12 902<br>Media:<br>EN 13752<br>CHEMICALS - AVAILABLE |

# ANNEX V: SOLUBILITY OF IRON OXIHYDROXIDES

Knowing the solubility of the media minerals at various pH levels can be useful when it comes to examining their behaviour during the passage of water or during base and acid rinsing.

Starting with the iron series, we shall examine four phases:

- Amorphous $Fe(OH)_3$ for precursors of the ferrihydrite-goethite group;
- $Fe(OH)_3$ ferrihydrite;
- $\alpha$-FeO.OH goethite;
- $\beta$-FeO.OH Akaganeite.

## - Amorphous $Fe(OH)_3$

1st reaction:
$Fe(OH)_{3am} \rightarrow Fe^{3+}_{aq} + 3OH^-_{aq}$
To show the influence of pH, this can be written
$Fe(OH)_{3am} + 3H^+_{aq} \Leftrightarrow Fe^{3+}_{aq} + 3H_2O_{liq}$

2nd reaction:
$Fe(OH)_{3am} \rightarrow FeOH^{2+}_{aq} + 2OH^-_{aq}$
which can be written
$Fe(OH)_{2am} + 2H^+_{aq} \rightarrow FeOH^{2+}_{aq} + 2H_2O_{liq}$

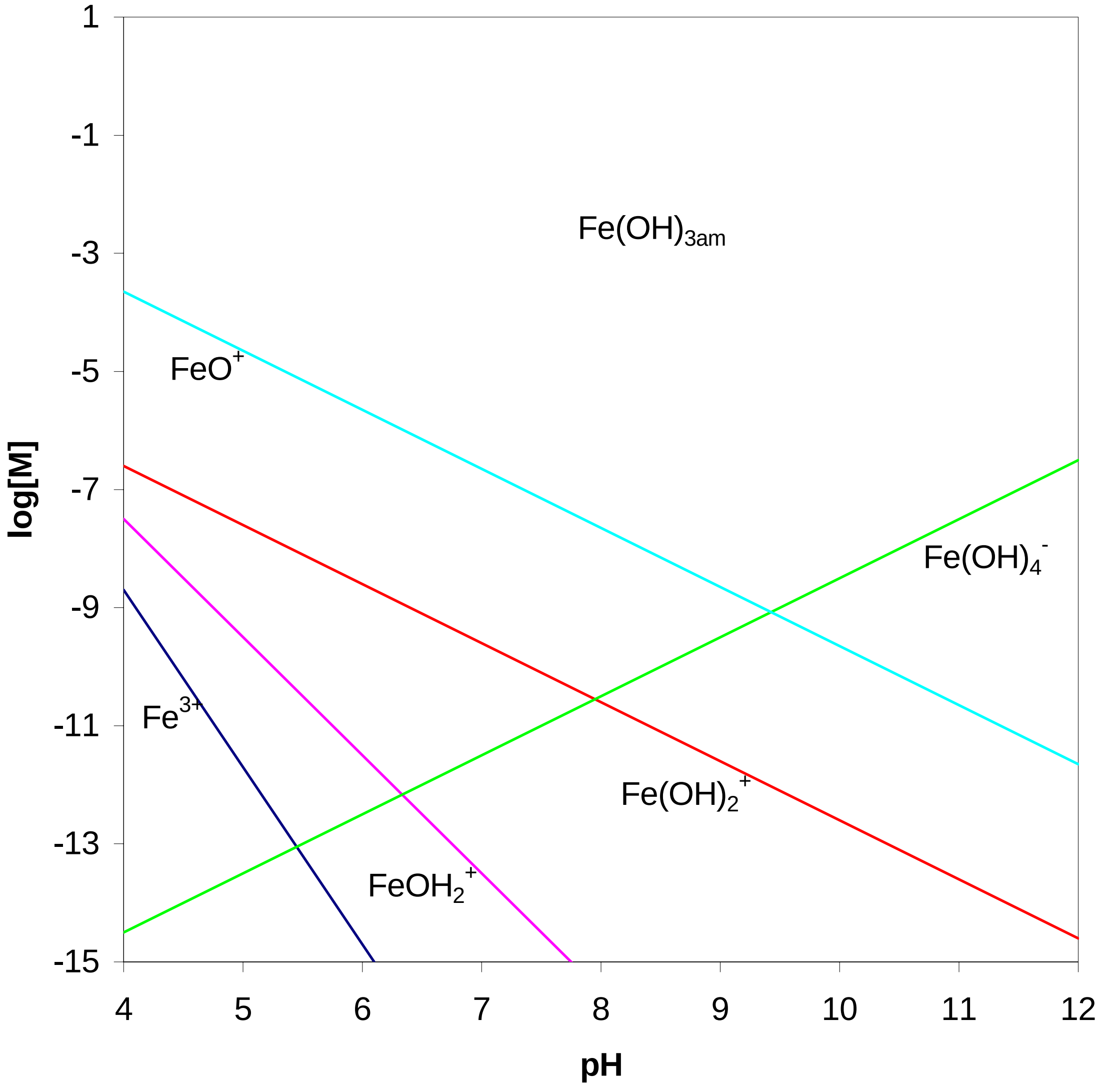
3rd reaction:
$Fe(OH)_{3am} \Leftrightarrow Fe(OH)^+_{2aq} + OH^-_{aq}$
or $Fe(OH)_{3am} + H^+_{aq} \Leftrightarrow Fe(OH)^+_{2aq} + H_2O_{liq}$

4th reaction:
$Fe(OH)_{3am} + OH^-_{aq} \Leftrightarrow Fe(OH)^-_{4aq}$
or alternatively $Fe(OH)_{3am} + H_2O_{liq} \Leftrightarrow Fe(OH)^-_{4aq} + H^+_{aq}$

5th reaction:
$Fe(OH)_{3am} + H^+_{aq} \rightarrow FeO^+_{aq} + 2H_2O_{liq}$

These five equilibrium equations form the basis for the solubility diagram for amorphous $Fe(OH)_3$. This is illustrated in figure 5.4.1.

**Figure 5.4.1**

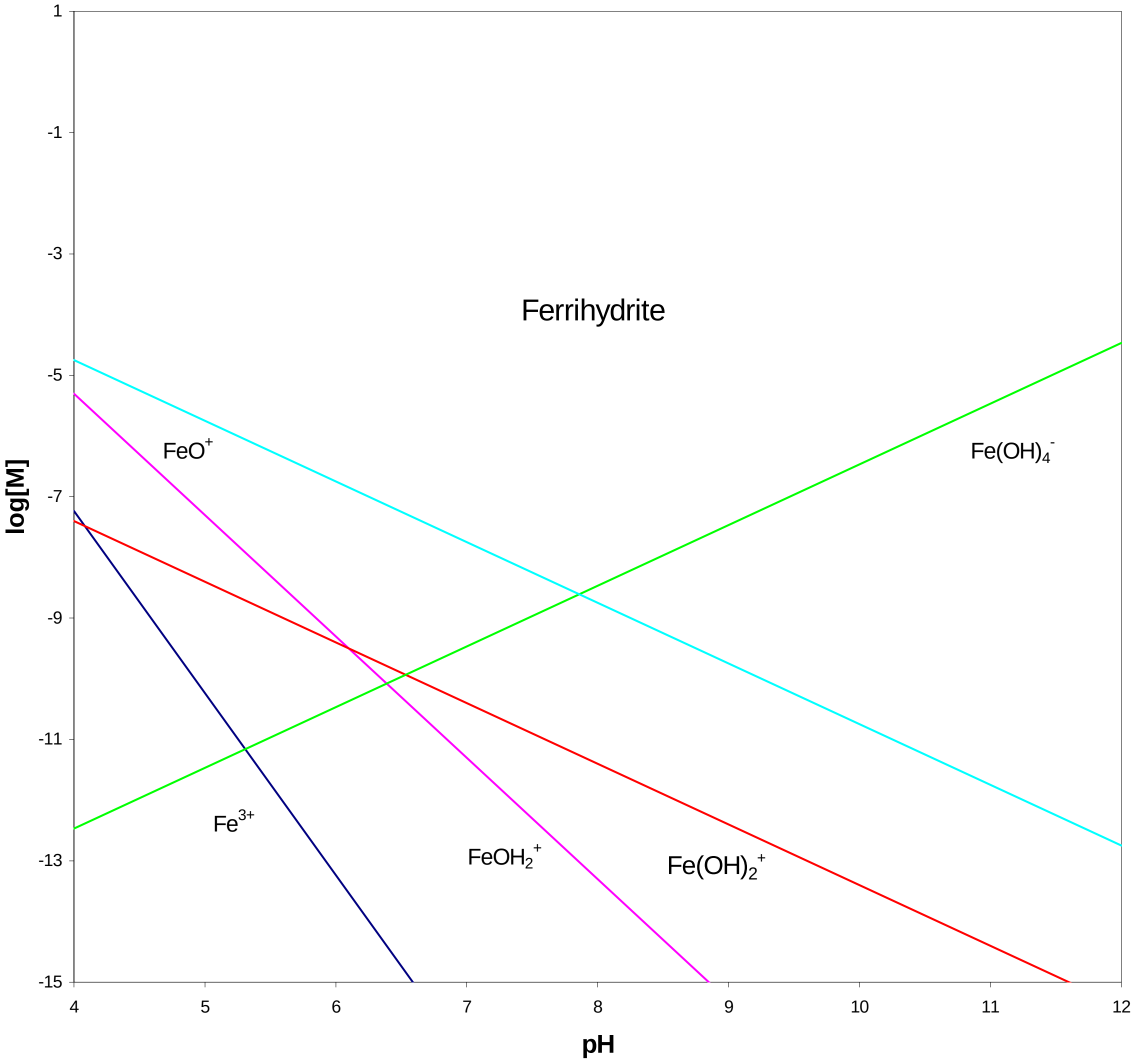


Minimum solubility occurs quite high up the pH scale (≈9.3) for a dissolved iron content of $\pm 10^{-9}$ moles/l.
In the filter pH zones, the content at equilibrium is higher.
Thus when pH=7.5, the iron concentration is $10^{-7.2}$ moles/l.

### - Ferrihydrite

With ferrihydrite, the same reactions produce a slightly different graph due to ferrihydrite's different Gibbs thermodynamic potential.

Figure 6.5.2



Minimum solubility has moved towards more neutral pH levels (≈7.8).

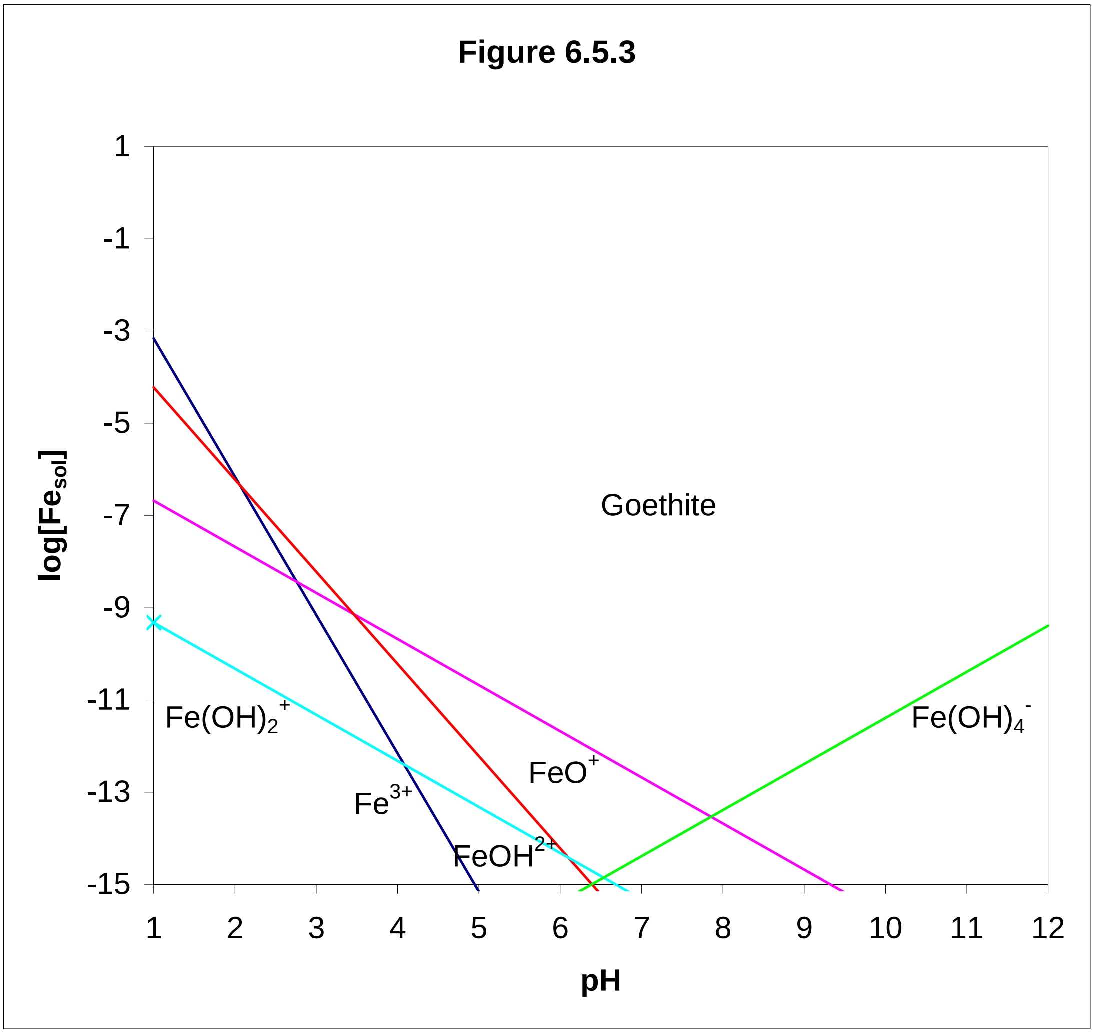
### - Solubility of goethite (α-FeO.OH)

The reactions are as follows:

1) $\alpha\text{-FeO.OH}_{(s)} + 3H^+_{aq} \Leftrightarrow Fe^{3+}_{aq} + 2H_2O_{liq} : K_1$
2) $\alpha\text{-FeO.OH}_{(s)} + H^+_{aq} \Leftrightarrow FeO^+_{aq} + H_2O_{liq} : K_2$
3) $\alpha\text{-FeO.OH}_{(s)} + 2H^+_{aq} \Leftrightarrow FeOH^{2+}_{aq} + H_2O_{liq} : K_3$
4) $\alpha\text{-FeO.OH}_{(s)} + H^+_{aq} \Leftrightarrow Fe(OH)^+_{2aq} : K_4$
5) $\alpha\text{-FeO.OH}_{(s)} + 2H_2O_{liq} \Leftrightarrow Fe(OH)^-_{4aq} + H^+_{aq} : K_5$
6) $\alpha\text{-FeO.OH}_{(s)} \Leftrightarrow FeO_2{}^-_{aq} + H^+_{aq} : K_6$

Having calculated the equilibrium equations based on the reagents' Gibbs free energies, we can produce the solubility diagram for goethite according to pH.

This is shown in figure 6.5.3 below.



Goethite is minimally soluble when the pH is approximately 7.8 with a dissolved iron content of around $10^{-13.5}$moles/l.

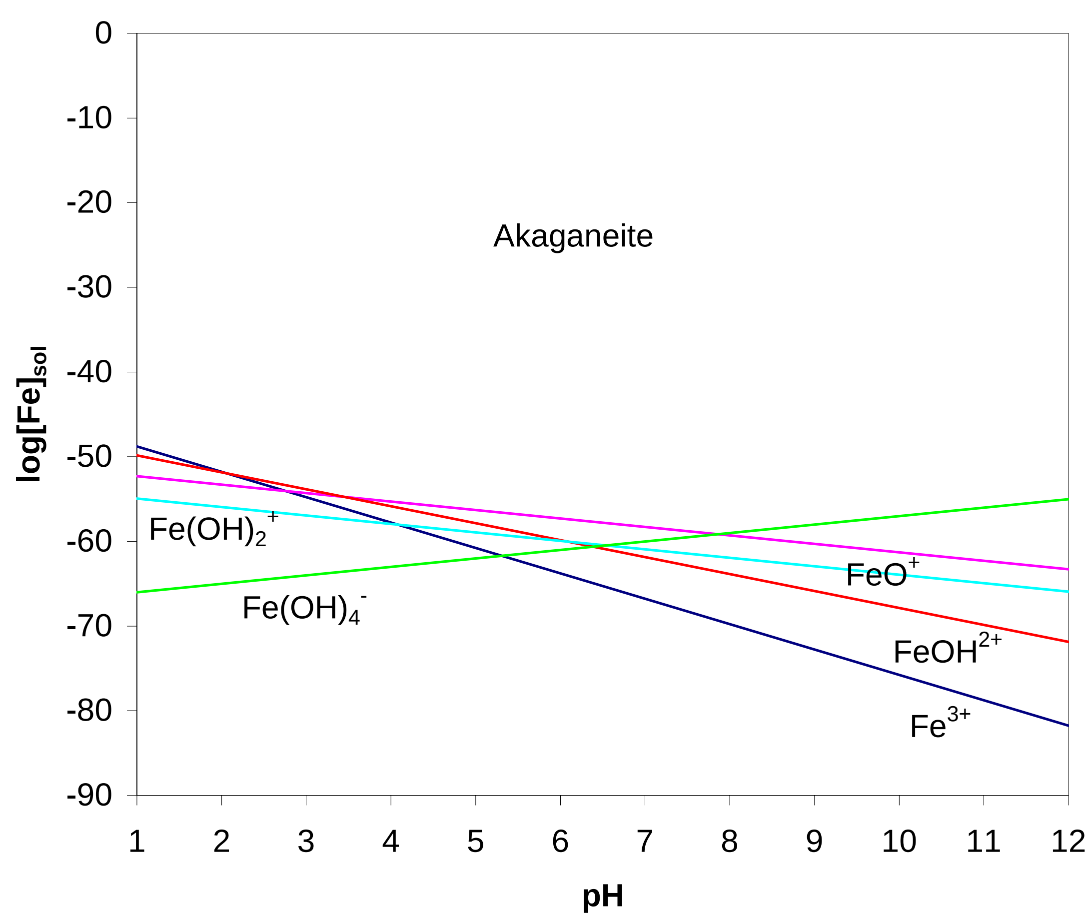
It is therefore less soluble than the amorphous phase and the less well crystallised intermediary phases.

### - Solubility of Akaganeite (β-FeO.OH)

The reactions are similar to those of goethite; they simply need to be recalculated using the Gibbs free energy of formation for Akaganeite instead of goethite.

The result of the calculation is contained in the solubility diagram in figure 6.5.4 below.

## Figure 6.5.4



Note that Akaganeite is much less soluble than the others. This makes it well-suited for capturing in its tubes but not suitable for providing Mn lower down in the filter. Hence it is predominantly an 'adsorbent' mineral.

We shall now examine the overall solubility of various manganese oxyhydroxides.

## ANNEX VI : EUROPEAN STANDARDS AND APPROVAL SCHEMES FOR MATERIALS AND PRODUCTS IN CONTACT WITH DRINKING WATER

### CEN/TC 164 - Published EN Standards

In order to facilitate standardised applications, the filter material must correspond to the relevant norms. The general requirements for filter materials are determined in the European Standards. The following standards apply:

**EN 12901 – Products used for treatment of water intended for human consumption – Inorganic supporting and filtering materials – Definitions**

- It concerns the definition of particle size grading of granular materials, density, porosity, mechanical properties, hydraulic properties, chemical properties, appearance, precision and reproducibility,

- **EN 12902 – Products used for the treatment of water intended for human consumption – Inorganic supporting and filtering materials – Methods of test**
    - It concerns test methods for determining the physico-chemical characteristics of inorganic supporting and filtering materials, especially leaching test available for all kind of media.

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**EN 13752: 2003 - Products used for treatment of water intended for human consumption: Manganese dioxide**

- it describes the characteristics and specifies obligation and relevant analytical methods for the use of manganese dioxide. The standard gives general information about origin (natural) and process of manufacturing and the identification and commercial name of manganese dioxide: Manganese(IV) oxide, pyrolusite. A footnote reminds “manganese dioxide ores differ widely in their commercial composition depending on their origin. Most are composed of manganese dioxide together with silica, alumina, iron oxide and numerous other elements present in varying proportions.” Point A 3.6 of standard focus on secondary effects when water contains more than 0.2 mg/l manganese: “the sand in which the manganese dioxide 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

**EN 14368: 2003 : Products used for treatment of water intended for human consumption - Manganese dioxide coated on limestone**

- Standard applies to manganese dioxide coated on limestone used for water treatment. The chemical name is manganese dioxide on limestone support material and synonyms are: Manganese(IV) oxide, pyrolusite on support material ($MnO_2$ and $CaCO_3$). Annexe A of standard specifies that the raw material is manganese dioxide according with EN 13752, which is suitable for use as catalytic filtration material, and calcium carbonate in accordance with

EN 1018. According to annex A, one can put this manganese dioxide in the fourth category [MnO2 coated (synthetic].

**EN 14369 : 2003 - Products used for treatment of water intended for human consumption - Iron-coated granular activated alumina**

- Standard applies to iron-coated granular activated alumina, produced from aluminium hydroxide complying with EN 13753 coated with iron using iron (III) sulphate conforming to EN 890. It can be used to remove fluoride (F) and (As) arsenate.

**EN 15029 : 2006 : - Products used for treatment of water intended for human consumption - Iron (III) hydroxide oxide**

- Standard applies to synthetic oxyhydroxide of iron sometimes called Goethite, Akaganeite.

**EN 12911 [09-2006]: - Products used for treatment of water intended for human consumption - Manganese greensand**

- Standard applies to manganese greensand ($MnO_2$ coated synthetic). The chemical name is manganese oxide coated zeolite (Glauconite) and synonyms are : manganese greensand, manganese zeolite, ferro sand, greensand.. According to annex A, the raw material is natural zeolite (Glauconite) and manganese dioxide obtain by manufacturing. One can put this manganese greensand in the fourth category [MnO2 coated (synthetic].

The above norms form the prerequisite for a technically appropriate application and for the guarantee that there is no risk for the dispensed mineral water with this treatment.
As well as the composition of the filter material, it is crucial which substances are yielded from the filter material to the water. Through elution (leaching test), a minimisation of risks and an appraisal should be able to be carried out with standardised methods.

## European and national approval schemes for materials and products in contact with drinking water

### - National standards

The EU Directive on the quality of water intended for human consumption (98/83/EC) has been incorporated in national legislation in member states. Article 10 of the Directive has provisions for materials and chemicals in contact with water, stating that they should not be used "*in concentrations higher than is necessary for the purpose of their use and do not, either directly or indirectly, reduce the protection of human health provided for in this Directive*". The water quality parameters (Parametric Values, PVs) in Annex 1 of the Directive related mainly to raw water contaminants, but some are associated with materials and chemicals used in water treatment or distribution. For example the PV for acrylamide monomer is based on the use of polyacrylamide products for coagulation/flocculation and for waterworks sludge treatment.

In many member states there are arrangements for the approval of these products, to prevent adverse effects on drinking water quality with respect to health and aesthetic properties i.e appearance, taste and odour. These national schemes have evolved independently, so there are differences in the approaches used in each country. However, common features of all schemes are:

1. Provision of information by manufacturer on the chemical nature of the material or the materials from which it is made, and intended use of the product.
2. Identification of suitable test condition, and carrying out leaching tests.
3. Review of the test results against agreed standards and/or by an expert group.

The details of the tests vary from country to country, but the range of tests used may cover:

- aesthetic parameters (colour, turbidity, taste and odour),
- general hygiene (total organic carbon, chlorine demand),
- leaching of toxic materials - regulated parameters, chemicals used in the production or general scans for unexpected substances,
- microbial tests for enhancement of bacterial growth.

The leaching tests can also take into account the surface area in contact with the water, the type of water and hydraulic conditions/stagnation periods.

Some countries without any acceptance scheme accept approvals from other countries. However, historically there was little mutual acceptance of approval between member states, and suppliers had to submit their products for approval in each member state. Some harmonisation has been achieved with production of European Standards (ENs) for drinking water treatment chemicals, accepted by the regulatory authorities of some countries.

# ANNEX VII : DEMONSTRATION OF DOPING EFFECT ON THE REMOVAL OF IRON AND MANGANESE

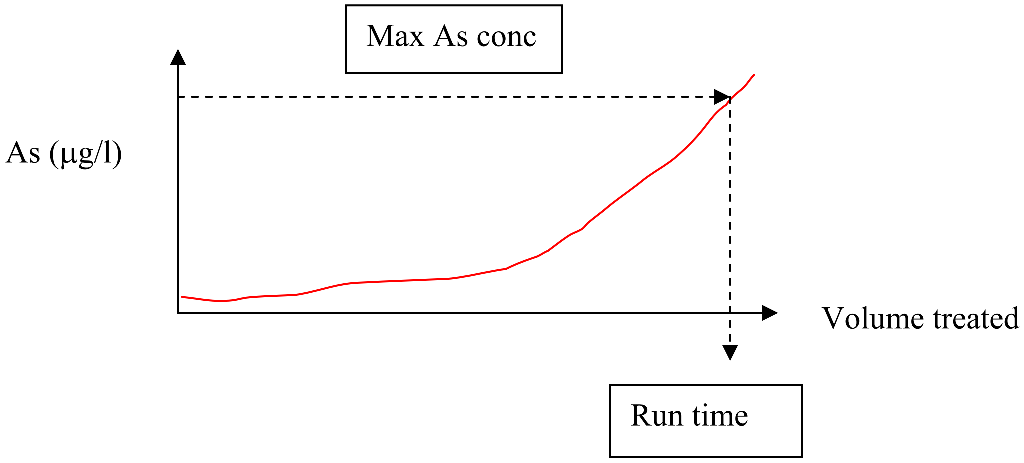
## spring E (Belgium report)

| Parameters | Spring E | |
|---|---|---|
| | Before treatment | After treatment |
| Cond µS/cm | 77 | 74 |
| Eh in Volt | 0,120/0,130 | 0,120/0,160 |
| pH | 5,20 | 5,60 |
| HCO3 mg/l | 6 | 7 |
| PO4 mg/l | - | - |
| Cl mg/l | 10,0 | 9,9 |
| NO3 mg/l | 5,7 | 5,6 |
| SO4 mg/l | 10,1 | 9,2 |
| F mg/l | <0,1 | <0,1 |
| Ca mg/l | 5,9 | 5,7 |
| Mg mg/l | 1,3 | 1,3 |
| Na mg/l | 5,8 | 5,8 |
| K mg/l | 0,7 | 0,7 |
| SiO2 mg/l | 7,2 | 7,1 |
| Al µg/l | 17 | <10 |
| As µg/l | - | - |
| Co µg/l | <1 | <1 |
| **Fe µg/l** | **90** | **<5** |
| Li µg/l | 2 | 2 |
| **Mn µg/l** | **77** | **8** |
| Ni µg/l | 3 | 4 |
| Sr µg/l | 12 | 12 |
| Zn µg/l | 3 | 14 |

Despite the low initial content of iron and manganese in water, their removal is successful by the doping mineral effect.

# ANNEX VIII : BREAKTHROUGH CURVE FOR AS REMOVAL USING IRON OXIHYDROXIDE (GEH)

The concentration of arsenic in the treated water increases over time, referred to as a breakthrough curve:



The run time will depend on:

- The arsenic concentration in the feed water and the target concentration in the treated water.
- Empty Bed Contact Time (EBCT): the volume of the media bed divided by the flowrate.
- pH of the water being treated.
- Grain size for the media.
- The oxidation state of the arsenic - arsenic is more readily adsorbed in the higher oxidation state As(V) compared with As (III).

# ANNEX IX : IMPACT ON NMW CHARACTERISTIC COMPOSITION

## Annex IX- 1 : Manganese oxihydroxide media (Belgium report)

| Parameters | **Spring A** | | | **Spring B** | | | **Spring C** | | | **Spring D** | | **Spring E** | | **Spring F** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before Fe treatment | After Fe treatment | After Mn treatment | Before Fe treatment | After Fe treatment | After Mn treatment | Before Fe treatment | After Fe treatment | After Mn treatment | Before Mn treatment | After Mn treatment | Before Mn treatment | After Mn treatment | Before Mn treatment | After Mn treatment | After As treatment with $MnO_2$ | After As treatment with FeOOH |
| Cond µS/cm | | | | 147 | 127 | 124 | 51 | 48 | 40 | 503 | 503 | 77 | 74 | 500 | 532 | 503 | 495 |
| Eh in Volt | -0,280 | 0,200 | | 0,030/0,100 | 0,160 | 0,200 | | 0,150/0,300 | 0,150/0,300 | - | - | 0,120/0,130 | 0,120/0,160 | 0,020 | 0,160/0,230 | 0,280 | |
| pH | 6,40 | 6,60 | 7,00 | 6,24 | 6,02 | 6,80 | 5,80 | 6,35 | 6,30 | 7,20 | 7,15 | 5,20 | 5,60 | 7,74 | 7,77 | 7,71 | 7,76 |
| **$HCO_3$ mg/l** | 205 | **160** | **149** | 88 | **67** | **65** | **19** | **17** | **13** | **320** | **315** | **6** | **7** | **157** | **165** | **156** | **163** |
| $PO_4$ mg/l | 0,32 | 0,12 | 0,10 | 0,07 | - | - | - | - | - | <0,05 | <0,05 | - | - | | <0,05 | <0,05 | <0,06 |
| **Cl mg/l** | 3,8 | **3,9** | **4,6** | 9,5 | **9,5** | **9,5** | **2,8** | **3,9** | **3,4** | **8,1** | **8,1** | **10,0** | **9,9** | **4,1** | **4,3** | **4,4** | **4,4** |
| $NO_3$ mg/l | <0,2 | <0,2 | <0,2 | 0,5 | 0,5 | 0,5 | 0,3 | 0,5 | 0,5 | 0,6 | 0,6 | 5,7 | 5,6 | 0,3 | <0,1 | <0,1 | <0,1 |
| **$SO_4$ mg/l** | 3,8 | **3,6** | **4,1** | 6,5 | **6,5** | **6,5** | **1,9** | **6,7** | **5,3** | **11,2** | **11,2** | **10,1** | **9,2** | **155,0** | **157,0** | **153,0** | **158,0** |
| F mg/l | 0,2 | - | - | - | - | - | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | <0,1 | 1,9 | 1,9 | 1,7 | 1,9 |
| **Ca mg/l** | 20,5 | **20,2** | **19,2** | 10,4 | **10,3** | **10,2** | **4,8** | **4,2** | **3,4** | **102,0** | **102,0** | **5,9** | **5,7** | **95,0** | **104,0** | **101,0** | **95,0** |
| **Mg mg/l** | 18,3 | **19,1** | **17,4** | 6,2 | **6,1** | **6,1** | **1,8** | **1,6** | **1,5** | **3,5** | **3,5** | **1,3** | **1,3** | **12,6** | **13,1** | **13,3** | **13,0** |
| **Na mg/l** | 7,7 | **8,0** | **7,7** | 7,7 | **7,7** | **7,7** | **3,0** | **2,3** | **2,2** | **5,2** | **5,2** | **5,8** | **5,8** | **3,1** | **3,4** | **3,3** | **3,4** |
| **K mg/l** | 1,3 | **1,3** | **1,3** | 1,0 | **0,9** | **0,9** | **0,3** | **0,2** | **0,2** | **0,7** | **0,7** | **0,7** | **0,7** | **1,4** | **1,4** | **1,3** | **1,6** |
| $SiO_2$ mg/l | 21,3 | 19,3 | 18,6 | 13,1 | 12,2 | 12,1 | 8,2 | 6,1 | 5,8 | 8,2 | 8,2 | 7,2 | 7,1 | 10,4 | 10,4 | 10,2 | 4,8 |
| Al µg/l | 103 | 103 | 98 | 43 | 5 | 7 | - | <10 | <10 | 20 | 20 | 17 | <10 | 12,0 | 9,0 | <10 | <10 |
| As µg/l | <1 | <1 | <1 | <1 | - | - | - | - | - | <1 | <1 | - | - | 12,0 | 13,0 | <3 | <3 |
| Co µg/l | 7 | <2 | <2 | 4 | 4 | <1 | - | - | - | <2 | <2 | <1 | <1 | <1 | <1 | <1 | <1 |
| Fe µg/l | 29500 | 22 | 11 | 9170 | 58 | <5 | 2000 | <5 | <5 | <10 | <10 | 90 | <5 | 10,0 | <5 | <5 | <5 |
| Li µg/l | 78 | 70 | 67 | 61 | 61 | 61 | 10 | 13 | 12 | 5 | 5 | 2 | 2 | 9,0 | 8,0 | 9,0 | 9,0 |
| Mn µg/l | 1500 | 8 | <1 | 329 | 298 | 2 | 58 | 59 | <1 | 320 | <15 | 77 | 8 | 67,0 | <3 | <3 | <3 |
| Ni µg/l | 17 | <3 | <3 | 8 | 9 | 3 | - | <2 | - | <3 | <3 | 3 | 4 | <2 | <2 | <2 | <2 |
| Sr µg/l | 27 | 25 | 24 | 19 | 18 | 18 | 6 | 6 | - | 90 | 90 | 12 | 12 | 865,0 | 820,0 | 861,0 | 88§ |
| Zn µg/l | 14 | <5 | <5 | 22 | 40 | <3 | 6 | 6 | - | <5 | <5 | 3 | 14 | 105,0 | 110,0 | 18,0 | 68,0 |

- not analysed

## Annex IX – 2 : Effect on silica when oxihydroxide of iron is used (Belgium report)

| water types | As (µg/l) |  | $SiO_2$ (mg/l) |  |
|---|---|---|---|---|
|  | before | after | before | After (3 steps) |
| $Na\text{-}HCO_3$ type sodium bicarbonate pH=7,20 | 35 | <2 | 13,3 | 12,6-13,4-13,4 |
| $Ca\text{-}HCO_3$ sparkling calcium bicarbonate pH=5,9 | 19 | <1 | 91 | 85-87-85 |
| Oligominéral pH= 8,0 | 19 | <1 | 5,1 | 3,9 |
| F type spring after demanganisation without $CO_2$ pH=7,76 | 10 to 12 | 2 to 4 | 10,3 | 4,57 to 5,84 |
| as above with $CO_2$ pH=6 | 10 to 12 | 2 to 4 | 10,3 | 8,22 to 11,17 |

# ANNEX X : IMPACT ON NMW CHARACTERISTIC COMPOSITION
## Iron oxihydroxide media (GEH)

### Annex X-1 : Spring 1 Na-HCO3 water (Italian report)

Chemical composition of the unfiltered and filtered Na-$HCO_3$ natural mineral water. The characterizing compounds are given in red. Filter material is GEH®. “Total variation” is filtered water (95264 BV) versus unfiltered water.

| Parameter | Unit | unfiltered water | filtered water | filtered water | filtered water | total variation |
|---|---|---|---|---|---|---|
| | | 23.10.01 | 21.11.01 | 16.01.02 | 21.11.02 | (%) |
| Bed volume | BV | | 6875 | 20379 | 95264 | |
| Specific electric conductivity | µS/cm | 1071.00 | 1070.00 | 1086.00 | 1094.00 | +2.2 |
| pH | | 7.19 | 7.24 | 7.20 | 7.25 | +0.8 |
| $Ca^{2+}$ | mg/L | 80 | 77 | 78 | 81 | +1.3 |
| $Mg^{2+}$ | mg/L | 21.6 | 22.4 | 24.7 | 22.9 | +6.0 |
| $Na^+$ | mg/L | 130.0 | 128.5 | 130.0 | 131.6 | +1.2 |
| $K^+$ | mg/L | 6.96 | 7.09 | 7.30 | 6.94 | -0.3 |
| $Fe_{tot}$ | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | |
| Mn | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | |
| $SO_4^{2-}$ | mg/L | 139 | 137 | 136 | 144 | +3.6 |
| $HCO_3^-$ | mg/L | 425 | 425 | 430 | 432 | +1.7 |
| $Cl^-$ | mg/L | 59.6 | 60.0 | 59.0 | 60.0 | +0.7 |
| $PO_4^{3-}$ | mg/L | <0.01 | <0.01 | <0.01 | <0.01 | |
| $SiO_2$ | mg/L | 13.3 | 12.6 | 13.4 | 13.4 | +0.8 |
| $NO_3^-$ | mg/L | 1.4 | 1.4 | 1.4 | 1.3 | -7.1 |
| Al | µg/L | 7 | 3 | 3 | 3 | -57.1 |
| As | µg/L | 35 | <2 | <2 | <2 | -100 |
| Ba | µg/L | 38 | 39 | 38 | 38 | 0 |
| B | µg/L | 277 | 256 | 264 | 265 | -4.3 |
| Br | µg/L | 577 | 558 | 644 | 638 | +10.6 |
| $F^-$ | µg/L | 466 | 476 | 498 | 545 | +16.9 |
| Li | µg/L | 343 | 431 | 387 | 394 | +14.9 |
| Sr | µg/L | 1760 | 1840 | 1650 | 1700 | -3.4 |

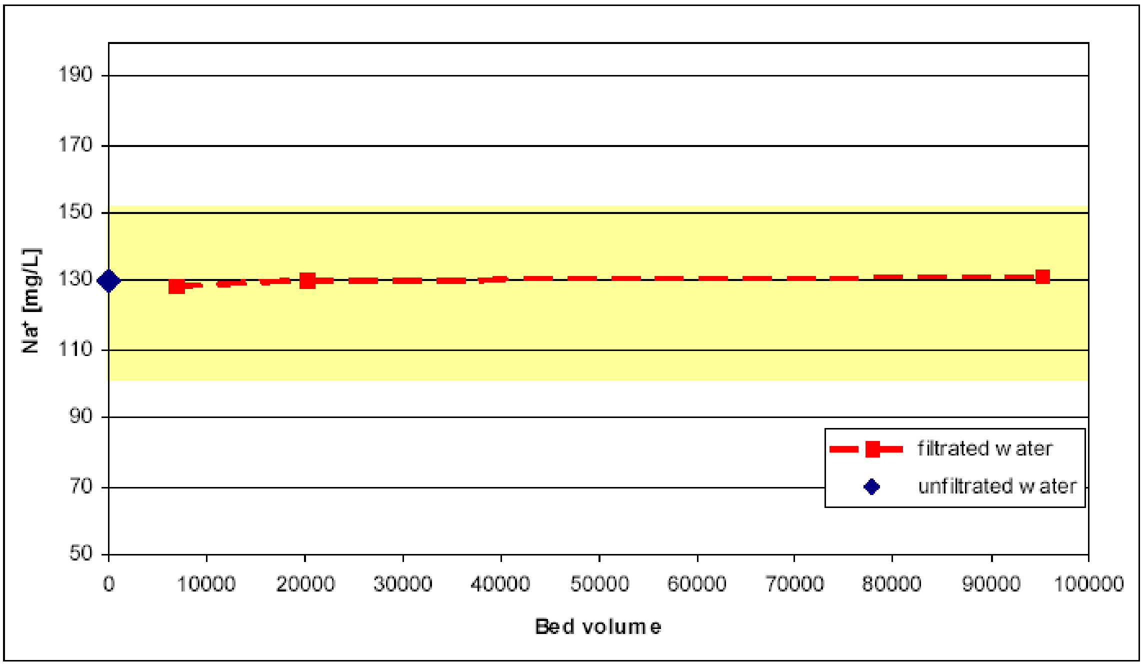


Fig. 9. $Na^+$ plotted versus bed volumes. $Na^+$ concentration of the filtered water is constant and corresponds to that of the unfiltered water.

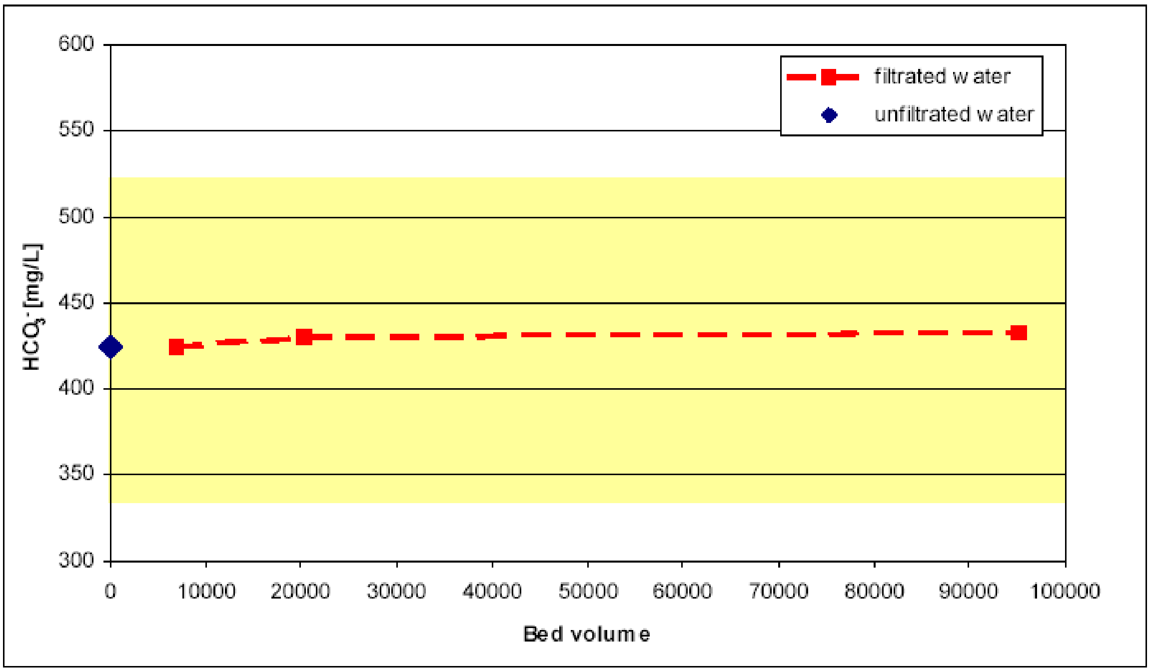


Fig.10. $HCO_3^-$ plotted versus bed volumes. $HCO_3^-$ concentration of the filtered water is constant and corresponds to that of the unfiltered water.

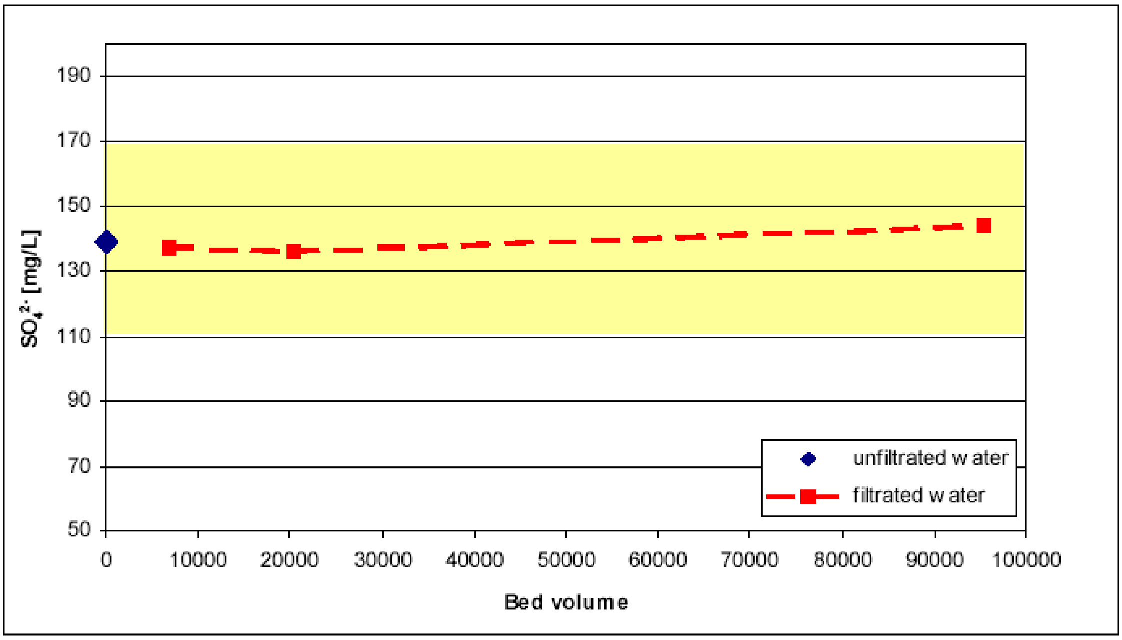


Fig. 12. [$SO_4^{2-}$] plotted versus bed volumes. The $SO_4^{2-}$ concentration of the filtered water is constant and corresponds to that of the unfiltered water.

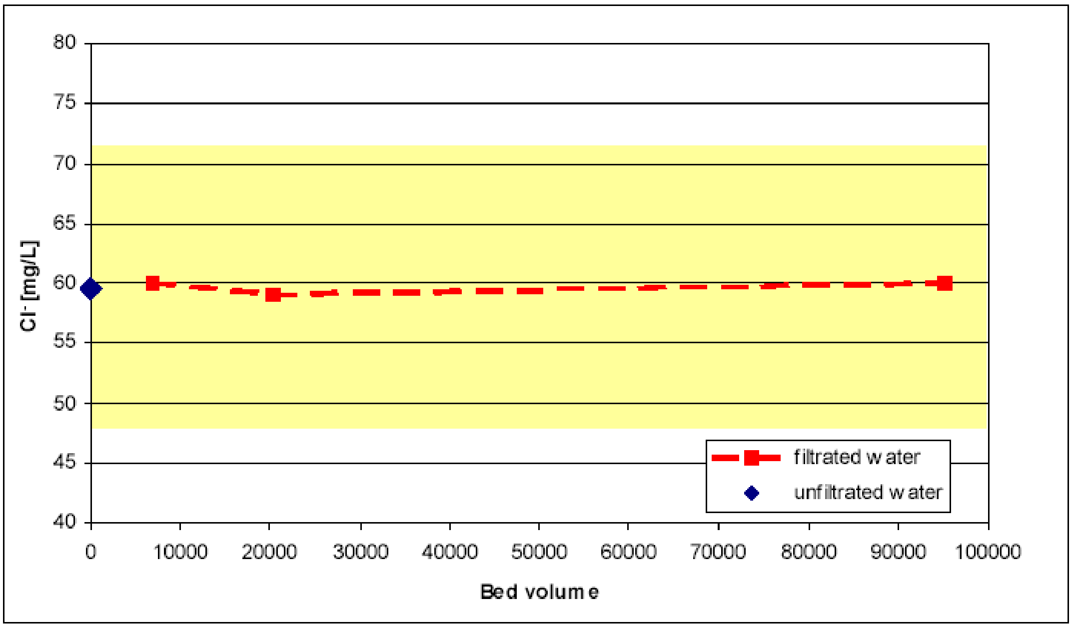


Fig. 13. [$Cl^-$] plotted versus bed volumes. The $Cl^-$ concentration of the filtered water is constant and corresponds to that of the unfiltered water.

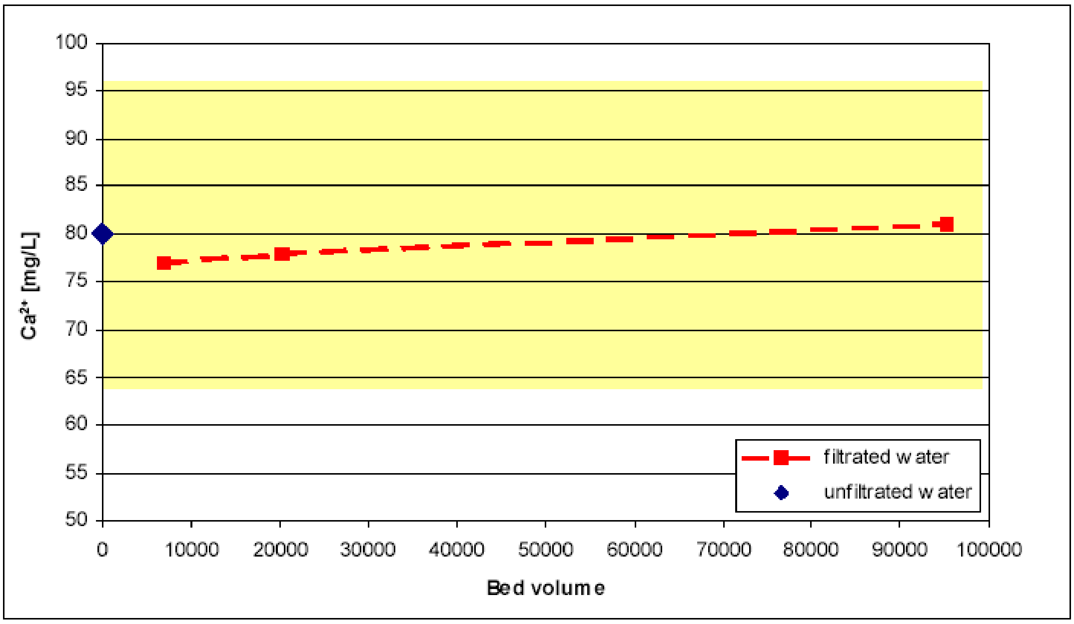


Fig.15. [$Ca^{2+}$] plotted versus bed volumes. The $Ca^{2+}$concentration of the mineral water is not changed during filtration with GEH®.

## Annex X-2 : Ca-HCO3 water (Italian report)

Chemical composition of the Ca-$HCO_3$ natural mineral water before and after filtration with GEH®.

| Parameter | Unit | unfiltered water | filtered water | unfiltered water | filtered water |
|---|---|---|---|---|---|
| | | 17.02.03 | 17.02.03 | 11.03.03 | 11.03.03 |
| Temperature | °C | n.d. | n.d. | n.d. | n.d. |
| pH (18°C) | | 5.9 | 6.0 | 5.92 | 5.89 |
| spec. elec. conductivity | µS/cm | 898 | 898 | 900 | 900 |
| dry residue (180°C) | mg/L | 603 | 613 | 609 | 607 |
| $O_2$ | mg/L | 0.5 | 0.5 | 0.5 | 0.5 |
| **$CO_2$** | **mg/L** | **1050** | **1050** | **1050** | **1050** |
| $SiO_2$ | mg/L | 91 | 85 | 87 | 85 |
| **$HCO_3^-$** | **mg/L** | **409** | **420** | **405** | **410** |
| $Cl^-$ | mg/L | 49 | 49 | 49 | 49 |
| $SO_4^{2-}$ | mg/L | 29 | 28 | 28 | 28 |
| $Na^+$ | mg/L | 55 | 57 | 55 | 56 |
| $K^+$ | mg/L | 67 | 68 | 66 | 68 |
| **$Ca^{2+}$** | **mg/L** | **75** | **74** | **75** | **75** |
| $Mg^{2+}$ | mg/L | 19.9 | 20.4 | 20 | 20 |
| $Fe_{total}$ | mg/L | 0.005 | 0.01 | 0.005 | 0.03 |
| $NH_4^+$ | mg/L | < 0.02 | <0.02 | <0.02 | <0.02 |
| P total | mg/L | 0.18 | 0.02 | 0.2 | 0.02 |
| $S^{2-}$ | mg/L | <0.02 | <0.02 | <0.02 | <0.03 |
| Sr | mg/L | 0.8 | 0.8 | 0.8 | 0.8 |
| Li | mg/L | 0.12 | 0.12 | 0.1 | 0.11 |
| Al | mg/L | <0.02 | <0.02 | <0.02 | <0.02 |
| $Br^-$ | mg/L | <0.05 | <0.05 | <0.05 | <0.05 |
| $I^-$ | mg/L | <0.01 | <0.01 | <0.01 | <0.01 |
| As | mg/L | 0.019 | <0.001 | 0.0156 | <0.001 |
| Ba | mg/L | 0.1 | 0.1 | 0.1 | 0.1 |
| B | mg/L | 0.94 | 1 | 0.83 | 0.94 |
| Cd | mg/L | 0.002 | 0.0017 | 0.002 | 0.0018 |
| Cr | mg/L | <0.05 | <0.05 | <0.05 | <0.05 |
| Cu | mg/L | 0.015 | 0.015 | 0.015 | 0.015 |
| $CN^-$ | mg/L | <0.01 | <0.01 | <0.01 | <0.01 |
| $F^-$ | mg/L | 1.05 | 0.9 | 1 | 1 |
| Pb | mg/L | 0.011 | 0.011 | 0.011 | 0.011 |
| Mn | mg/L | 0.2 | 0.2 | 0.2 | 0.2 |
| Hg | mg/L | <0.001 | <0.001 | <0.001 | <0.001 |
| $NO_3^-$ | mg/L | 8 | 8 | 8 | 7.8 |
| $NO_2^-$ | mg/L | <0.02 | <0.02 | <0.02 | <0.02 |
| Se | mg/L | <0.01 | <0.01 | <0.01 | <0.01 |
| Surfactants (MABS) | □g/L | <50 | <50 | <50 | <50 |
| Mineral oils-hydrocarb. | □g/L | <10 | <10 | <10 | <10 |
| Benzo(a)pirene | □g/L | <0.003 | <0.003 | <0.003 | <0.003 |
| Benzo(b)fluorantene | □g/L | <0.006 | <0.006 | <0.006 | <0.006 |
| Benzo(k)fluorantene | □g/L | <0.006 | <0.006 | <0.006 | <0.006 |
| Benzo(ghi)perylene | □g/L | <0.006 | <0.006 | <0.006 | <0.006 |

| | | | | | |
|---|---|---|---|---|---|
| Dibenzo(a,h)anthracene | μg/L | <0.006 | <0.006 | <0.006 | <0.006 |
| Indeno(1,2,3-cd)pirene | μg/L | <0.006 | <0.006 | <0.006 | <0.006 |
| Pesticides | μg/L | <0.05 | <0.05 | <0.05 | <0.05 |
| Organohalogenated compounds | μg/L | <0.5 | <0.5 | <0.5 | <0.5 |

## Annex X-3 : Oligomineral water (Italian report)

Chemical composition of the oligomineral natural water before and after filtration with GEH.

| | | unfiltered water | filtered water | unfiltered water | filtered water | unfiltered water | filtered water | unfiltered water | filtered water |
|---|---|---|---|---|---|---|---|---|---|
| | | 07.07.04 | 07.07.04 | 04.08.04 | 04.08.04 | 01.09.04 | 01.09.04 | 07.10.04 | 07.10.04 |
| pH (18°C) | | 8 | 8 | 7.9 | 7.9 | 8 | 8 | 7.8 | 7.7 |
| spec. elec. conductivity | µS/cm | 173 | 173 | 173 | 173 | 152 | 150 | 152 | 155 |
| dry residue (180°C) | mg/L | 122 | 121 | 119 | 118 | 105 | 104 | 107 | 108 |
| $O_2$ | mg/L | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| $SiO_2$ | mg/L | 5.1 | 3.9 | 4.6 | 3.4 | 4.2 | 3.7 | 4.5 | 4.5 |
| $HCO_3^-$ | mg/L | 75.4 | 75.5 | 70.9 | 71.4 | 70.4 | 70.3 | 67 | 68.3 |
| $Cl^-$ | mg/L | 0.5 | 0.5 | 0.6 | 0.5 | 0.7 | 0.6 | 0.6 | 0.6 |
| $SO_4^{2-}$ | mg/L | 38 | 38.2 | 37.4 | 37.5 | 28.9 | 28.9 | 31.7 | 31.5 |
| $Na^+$ | mg/L | 3.3 | 3.3 | 3 | 3 | 2.4 | 2.4 | 2.6 | 2.6 |
| $K^+$ | mg/L | 3.1 | 3.1 | 2.6 | 2.5 | 2.3 | 2.3 | 2.6 | 2.6 |
| $Ca^{2+}$ | mg/L | 29.7 | 29.7 | 29.5 | 29.3 | 25.7 | 25.7 | 26.5 | 26.8 |
| $Mg^{2+}$ | mg/L | 3.8 | 3.8 | 3.6 | 3.5 | 3.2 | 3.2 | 3.3 | 3.2 |
| $Fe_{total}$ | mg/L | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| $NH_4^+$ | mg/L | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| P total | mg/L | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| $S^{2-}$ | mg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Sr | mg/L | 0.15 | 0.15 | 0.15 | 0.15 | 0.12 | 0.12 | 0.12 | 0.12 |
| Li | mg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Al | mg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Br | mg/L | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| I | mg/L | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Sb | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| As | mg/L | 0.019 | <0.001 | 0.018 | <0.001 | 0.014 | <0.001 | 0.008 | <0.001 |
| Ba | mg/L | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| B | mg/L | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Cd | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Cr | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Cu | mg/L | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| CN | mg/L | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| F | mg/L | 0.6 | 0.6 | 0.5 | 0.5 | 0.4 | 0.4 | 0.5 | 0.5 |
| Pb | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Mn | mg/L | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Hg | mg/L | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 |
| Ni | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| $NO_3^-$ | mg/L | 1 | 1 | 1.2 | 1.2 | 1.4 | 1.4 | 1.3 | 1.4 |
| $NO_2^-$ | mg/L | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Se | mg/L | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |

## Annex X-4: Ion Balance High level mineralized water (German report)

**Typical results for removal arsenic with iron oxide filtration (GEH filter– material)**
**Sampling for analysis made during process for production**

| Results | | | |
|---|---|---|---|
| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
| pH-value | | 6,99 | 6,99 |
| Conductivity (25°C) | µS/cm | 2800 | 2810 |
| | | | |
| **Kations** | | | |
| | | | |
| Lithium (Li) | mg/l | 0,91 | 0,89 |
| Natrium (Na) | mg/l | 367 | 372 |
| Kalium (K) | mg/l | 20,6 | 20,5 |
| Ammonium ($NH_4$) | mg/l | < 0,02 | < 0,02 |
| Magnesium (Mg) | mg/l | 16,8 | 16,8 |
| Calcium (Ca) | mg/l | 164 | 163 |
| Strontium (Sr) | mg/l | 4,1 | 4,1 |
| Mangan (Mn) | mg/l | 0,052 | 0,048 |
| Eisen (Fe) | mg/l | 0,006 | < 0,005 |
| | | | |
| **Anions** | | | |
| | | | |
| Fluorid (F) | mg/l | 0,66 | 0,68 |
| Iodid (I) | mg/l | 0,019 | 0,019 |
| Bromid (Br) | mg/l | 1,8 | 1,8 |
| Chlorid (Cl) | mg/l | 740 | 741 |
| Nitrit ($NO_2$) | mg/l | < 0,005 | < 0,005 |
| Nitrat ($NO_3$) | mg/l | 2,3 | 2,1 |
| Sulfat ($SO_4$) | mg/l | 34 | 35 |
| Hydrogenphosphat ($HPO_4$) | mg/l | < 0,04 | < 0,04 |
| Hydrogencarbonat ($HCO_3$) | mg/l | 303 | 301 |
| Carbonat ($CO_3$) | mg/l | < 3 | < 3 |
| Hydrogensulfid (HS) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Undissociated substances** | | | |
| | | | |

| | | | |
|---|---|---|---|
| Kieselsäure ($H_2SiO_3$) | mg/l | 25,3 | 24,2 |
| Borsäure ($HBO_2$) | mg/l | 1,09 | 1,05 |

| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
|---|---|---|---|
| Total dissolved minerals | mg/l | 1680 | 1680 |
| | | | |
| **Dissolved gases** | | | |
| | | | |
| Kohlenstoffdioxid (CO2) | mg/l | 59 | 53 |
| | | | |
| **Evaporation residues** | | | |
| | | | |
| Abdampfrückstand bei 180°C | mg/l | 1700 | 1690 |
| Abdampfrückstand bei 260°C | mg/l | 1520 | 1520 |
| | | | |
| **Inorganic Compounds** | | | |
| | | | |
| Aluminium(Al) | mg/l | < 0,005 | < 0,005 |
| Arsen (As) | mg/l | 0,035 | 0,001 |
| Antimon (Sb) | mg/l | 0,001 | < 0,001 |
| Barium (Ba) | mg/l | 0,17 | 0,16 |
| Beryllium (Be) | mg/l | < 0,0005 | < 0,0005 |
| Blei (Pb) | mg/l | < 0,0005 | < 0,0005 |
| Bor (B) | mg/l | 0,27 | 0,26 |
| Cadmiun (Cd) | mg/l | < 0,0002 | < 0,0002 |
| Cäsium (Cs) | mg/l | 0,011 | 0,012 |
| Chrom (Cr) | mg/l | < 0,001 | < 0,001 |
| Kobalt (Co) | mg/l | < 0,001 | < 0,001 |
| Kupfer (Cu) | mg/l | < 0,001 | < 0,001 |
| Molybdän (Mo) | mg/l | < 0,001 | 0,011 |
| Nickel (Ni) | mg/l | 0,002 | 0,002 |
| Quecksilber (Hg) | mg/l | < 0,0001 | < 0,0001 |
| Rubidium (Rb) | mg/l | 0,036 | 0,037 |
| Selen (Se) | mg/l | < 0,0010 | < 0,0010 |
| Silber (Ag) | mg/l | < 0,0005 | < 0,0005 |

| | | | |
|---|---|---|---|
| Thallium (Tl) | mg/l | 0,004 | 0,003 |
| Titan (Ti) | mg/l | < 0,001 | < 0,001 |
| Uran (U) | mg/l | 0,0004 | 0,0004 |
| Vanadium (V) | mg/l | < 0,001 | < 0,001 |
| Zink (Zn) | mg/l | 0,17 | 0,11 |
| Zinn (Sn) | mg/l | < 0,001 | < 0,001 |
| Sulfid (S) | mg/l | < 0,005 | < 0,005 |
| Bromat ($BrO_3$) | mg/l | < 0,001 | < 0,001 |

## Annex X-5 : $Na^-Ca^-HCO_3^-SO_4$-Water and Co-Removal of some trace elements (German report)

**Typical results for removal arsenic with iron oxide filtration (GEH)**

**Sampling for analysis made during process for production**

**Results**

| **Parameter** | **Unit** | **Results** **before treatment** | **Results Filter 1** **after treatment** | **Results Filter 2** **after treatment** |
|---|---|---|---|---|
| pH-value | | 6,01 | 6,00 | 6,00 |
| Conductivity (25°C) | µS/cm | 1080 | 1100 | 1100 |
| **Kations** | | | | |
| Lithium (Li) | mg/l | 0,76 | 0,76 | 0,76 |
| Natrium (Na) | mg/l | 141 | 140 | 142 |
| Kalium (K) | mg/l | 11,0 | 10,8 | 11,0 |
| Ammonium ($NH_4$) | mg/l | 0,03 | < 0,02 | < 0,02 |
| Magnesium (Mg) | mg/l | 19,9 | 19,9 | 20,1 |
| Calcium (Ca) | mg/l | 96,3 | 95,3 | 93,4 |
| Strontium (Sr) | mg/l | 1,0 | 1,0 | 1,0 |
| Mangan (Mn) | mg/l | 0,24 | 0,23 | 0,23 |
| Eisen (Fe) | mg/l | 0,009 | 0,005 | < 0,005 |
| **Anions** | | | | |
| Fluorid (F) | mg/l | 1,5 | 1,4 | 1,4 |
| Iodid (I) | mg/l | < 0,005 | < 0,005 | < 0,005 |
| Bromid (Br) | mg/l | 0,06 | 0,05 | 0,06 |
| Chlorid (Cl) | mg/l | 14,9 | 14,7 | 14,8 |
| Nitrit ($NO_2$) | mg/l | < 0,005 | < 0,005 | < 0,005 |
| Nitrat ($NO_3$) | mg/l | 1,6 | 1,5 | 1,5 |
| Sulfat ($SO_4$) | mg/l | 116 | 117 | 114 |
| Hydrogenphosphat ($HPO_4$) | mg/l | < 0,04 | < 0,04 | < 0,04 |
| Hydrogencarbonat ($HCO_3$) | mg/l | 610 | 607 | 604 |
| Carbonat ($CO_3$) | mg/l | < 3 | < 3 | < 3 |
| Hydrogensulfid (HS) | mg/l | < 0,005 | < 0,005 | < 0,005 |
| **Undissociated substances** | | | | |
| Kieselsäure ($H_2SiO_3$) | mg/l | 52,8 | 50,0 | 47,3 |
| Borsäure ($HBO_2$) | mg/l | 1,22 | 1,13 | 1,13 |

| **Parameter** | **Unit** | **Results before treatment** | **Results Filter 1 after treatment** | **Results Filter 2 after treatment** |
|---|---|---|---|---|
| Total dissolved minerals | mg/l | 1070 | 1060 | 1050 |
| | | | | |
| **Dissolved gases** | | | | |
| | | | | |
| Kohlenstoffdioxid (CO2) | mg/l | 660 | 664 | 651 |
| | | | | |
| **Evaporation residues** | | | | |
| | | | | |
| Abdampfrückstand bei 180°C | mg/l | 719 | 736 | 722 |
| Abdampfrückstand bei 260°C | mg/l | 670 | 675 | 665 |
| | | | | |
| **Inorganic Compounds** | | | | |
| | | | | |
| Aluminium(Al) | mg/l | 0,005 | < 0,005 | < 0,005 |
| Arsen (As) | mg/l | 0,005 | < 0,001 | < 0,001 |
| Antimon (Sb) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Barium (Ba) | mg/l | 0,088 | 0,084 | 0,083 |
| Beryllium (Be) | mg/l | 0,0009 | < 0,0005 | < 0,0005 |
| Blei (Pb) | mg/l | < 0,0005 | < 0,0005 | < 0,0005 |
| Bor (B) | mg/l | 0,30 | 0,28 | 0,28 |
| Cadmiun (Cd) | mg/l | < 0,0002 | < 0,0002 | < 0,0002 |
| Cäsium (Cs) | mg/l | 0,008 | 0,008 | 0,008 |
| Chrom (Cr) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Kobalt (Co) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Kupfer (Cu) | mg/l | 0,001 | < 0,001 | < 0,001 |
| Molybdän (Mo) | mg/l | 0,002 | < 0,001 | < 0,001 |
| Nickel (Ni) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Quecksilber (Hg) | mg/l | < 0,0001 | < 0,0001 | < 0,0001 |
| Rubidium (Rb) | mg/l | 0,027 | 0,028 | 0,029 |
| Selen (Se) | mg/l | < 0,0010 | < 0,0010 | 0,0010 |
| Silber (Ag) | mg/l | < 0,0005 | < 0,0005 | < 0,0005 |
| Thallium (Tl) | mg/l | < 0,0002 | < 0,0002 | < 0,0002 |
| Titan (Ti) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Uran (U) | mg/l | 0,0030 | 0,0007 | < 0,0002 |
| Vanadium (V) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Zink (Zn) | mg/l | 0,34 | < 0,005 | 0,005 |
| Zinn (Sn) | mg/l | < 0,001 | < 0,001 | < 0,001 |
| Sulfid (S) | mg/l | < 0,005 | < 0,005 | < 0,005 |
| Bromat ($BrO_3$) | mg/l | < 0,001 | < 0,001 | < 0,001 |

| **Parameter** | **Unit** | **Results before treatment** | **Results Filter 1 after treatment** | **Results Filter 2 after treatment** |
|---|---|---|---|---|
| **Group Parameter** | | | | |
| | | | | |
| Spectral Absorption at 254 nm | 1/m | 0,68 | - | 0,48 |
| Spectral Absorption at 436 nm | 1/m | 0,10 | - | 0,08 |
| TOC | mg/l | 1,3 | 0,5 | 0,7 |
| Kohlenwasserstoffe nach H18 | mg/l | < 0,1 | - | < 0,1 |
| Cyanide (CN) | mg/l | < 0,005 | < 0,005 | < 0,005 |
| | | | | |
| **Polycyclic aromatic hydrocarbons** | | | | |
| | | | | |
| Fluoranthen | µg/l | < 0,002 | - | < 0,002 |
| Benzo(b)fluoranthen | µg/l | < 0,002 | - | < 0,002 |
| Benzo(k)fluoranthen | µg/l | < 0,002 | - | < 0,002 |
| Benzo(a)pyren | µg/l | < 0,002 | - | < 0,002 |
| Benzo(g,h,i)perylen | µg/l | < 0,002 | - | < 0,002 |
| Indeno(1,2,3-c,d)pyren | µg/l | < 0,002 | - | < 0,002 |
| | | | | |
| **Solvents** | | | | |
| Dichlormethan | µg/l | < 5 | - | < 5 |
| 1,1,1-Trichlorethan | µg/l | < 0,1 | - | < 0,1 |
| Trichlorethen | µg/l | < 0,1 | - | < 0,1 |
| Tetrachlorethen | µg/l | < 0,1 | - | < 0,1 |
| Tetrachlormethan | µg/l | < 0,1 | - | < 0,1 |
| | | | | |
| **Trihalomethanes (Haloforms)** | | | | |
| | | | | |
| Trichlormethan | µg/l | < 0,5 | - | < 0,5 |
| Bromdichlormethan | µg/l | < 0,1 | - | < 0,1 |
| Dibromchlormethane | µg/l | < 0,1 | - | < 0,1 |
| Tribrommethan | µg/l | < 0,1 | - | < 0,1 |
| Summe der Trihalogenmethane | µg/l | - | - | |
| | | | | |
| **Chlorinated Organic Compounds** | | | | |
| | | | | |
| cis-1,2-Dichlorethen | µg/l | < 5 | - | < 5 |
| Trans-1,2-Dichlorethen | µg/l | < 5 | - | < 5 |
| 1,1,2-Trichlorethan | µg/l | < 5 | - | < 5 |
| 1,2-Dichlorpropan | µg/l | < 5 | - | < 5 |

| **Parameter** | **Unit** | **Results**<br>**before treatment** | **Results Filter 1**<br>**after treatment** | **Results Filter 2**<br>**after treatment** |
|---|---|---|---|---|
| 1,3-Dichlorpropan | µg/l | < 5 | - | < 5 |
| | | | | |
| **Phenoles detected by GC** | | | | |
| | | | | |
| 2-Chlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 4-Chlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,4-Dichlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 3,5-Dichlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,3,5-Trichlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,4,6-Trichlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,3,4,6-Tetrachlorphenol | µg/l | < 0,1 | - | < 0,1 |
| 4-Chlor-3-methylphenol | µg/l | < 0,5 | - | < 0,5 |
| Pentachlorphenol | µg/l | < 0,1 | - | < 0,1 |
| Phenol | µg/l | < 0,5 | - | < 0,5 |
| 2-Methylphenol | µg/l | < 0,1 | - | < 0,1 |
| 3-Methylphenol | µg/l | < 0,1 | - | < 0,1 |
| 4- Methylphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,4-Dimethylphenol | µg/l | < 0,1 | - | < 0,1 |
| 3,4-Dimethylphenol | µg/l | < 0,1 | - | < 0,1 |
| 2,3,5-Trimethylphenol | µg/l | < 0,1 | - | < 0,1 |
| o-Phenylphenol | µg/l | < 0,5 | - | < 0,5 |
| | | | | |
| **Aromatic Hydrocarbon** | | | | |
| | | | | |
| Benzol | µg/l | < 1 | - | < 1 |
| Formaldehyd | µg/l | < 5 | < 5 | < 5 |
| | | | | |
| | | | | |
| | | | | |
| Radon-222 | Bq/l | 76 | 73 | 73 |
| Radium-226 | mBq/l | 29 | - | 20 |
| Radium-228 | mBq/l | 51 | - | 40 |

# ANNEX XI : IMPACT ON MICROBIOLOGY

## Annex XI-1 : Manganese dioxide filter systems: Microbiological results (German report)

| Mineralwater types | before | after | Colony counts | | E. coli | Coliforms | | Pseudomonas aeruginosa | Faecal streptococcus | sporulated sulphite-reducing anaerobes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20°C | 37°C | 250 ml | 250 ml | | 250 ml | 250 ml | 50 ml |
| 1 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 2 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 3 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 4 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 5 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 6 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |

## Annex XI-2 : Iron oxide filter systems: Microbiology results (German report)

| **Mineralwater types** | **before** | **after** | **Colony counts** | | **E. coli** | **Coliforms** | | **Pseudomonas aeruginosa** | **Faecal streptococcus** | **sporulated sulphite-reducing anaerobes** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **20°C** | **37°C** | **250 ml** | **250 ml** | | **250 ml** | **250 ml** | **50 ml** |
| 1 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 2 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 3 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 4 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 5 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |
| 6 | X | | 0 | 0 | negative | negative | | negative | negative | negative |
| | | X | 0 | 0 | negative | negative | | negative | negative | negative |

# ANNEX XII - COMPOSITION OF MEDIA

## Annex XII-1 : Analyses of filter material ROWA sorb iron oxide GEH (German report)

**- Main compounds of iron oxide**

| Parameter | Results ppm |
|---|---|
| Eisen (Fe) | Matrix |
| Schwefel (S) | 1700 |
| Mangan (Mn) | 1280 |
| Calcium (Ca) | 1160 |
| Silicium (Si) | 420 |
| Aluminium (Al) | 414 |

**- Trace compounds of iron oxide**

| Parameter | Results ppm |
|---|---|
| Natrium (Na) | 185 |
| Vanadium (V) | 160 |
| Magnesium (Mg) | 133 |
| Titan (Ti) | 110 |
| Chrom (Cr) | 65 |
| Nickel (Ni) | 53 |
| Kupfer (Cu) | 35 |
| Niob (Nb) | 32 |
| Phosphor (P) | 31 |
| Cobalt (Co) | 28 |
| Kalium (K) | <20 |
| Zink (Zn) | 17 |
| Bor (B) | 15 |
| Strontium (Sr) | 9,8 |
| Barium (Ba) | 4,3 |
| Molybdän (Mo) | 2,1 |

**- Traces below limit of quantification.**

| Parameter | Results ppm |
|---|---|
| Arsen (As) | <5 |
| Blei (Pb) | <1 |
| Wolfram (W) | <1 |
| Silber (Ag) | <1 |
| Rubidium (Rb) | <1 |
| Selen (Se) | <1 |
| Yttrium (Y) | <1 |
| Thallium (Tl) | <1 |

| | |
|---|---|
| Cer (Ce) | <1 |
| Antimon (Sb) | <1 |
| Lithium (Li) | <1 |
| Wismut (Bi) | <1 |
| Zirkonium (Zr) | <1 |
| Lanthan (La) | <1 |
| Zinn (Sn) | <1 |
| Cadmium (Cd) | <0,5 |

**- Traces below limit of quantification.**

| **Parameter** | **Results ppm** |
|---|---|
| Germanium (Ge) | <5 |
| Gold (Au) | <1 |
| Tellur (Te) | <1 |
| Uran (U) | <1 |
| Beryllium (Be) | <1 |
| Dysprosium (Dy) | <1 |
| Erbium (Er) | <1 |
| Europium (Eu) | <1 |
| Gallium (Ga) | <1 |
| Gadolinium (Gd) | <1 |
| Hafnium (Hf) | <1 |
| Holmium (Ho) | <1 |
| Indium (In) | <1 |
| Iridium (Ir) | <1 |
| Lutetium (Lu) | <1 |
| Osmium (Os) | <1 |
| Palladium (Pd) | <1 |
| Platin(Pt) | <1 |
| Rhenium (Re) | <1 |
| Rhodium (Rh) | <1 |
| Ruthenium (Ru) | <1 |
| Samarium (Sm) | <1 |
| Terbium (Tb) | <1 |
| Thorium (Th) | <1 |
| Thulium (Tm) | <1 |
| Ytterbium (Yb) | <1 |

## Annex XII-2 : Composition of manganese dioxide filter material “L standard“ (natural ore) (German report)

***matrix*** *manganese dioxide (81 %), iron oxide (10 %)*

### main compounds

| **Parameter** | **Results ppm** |
|---|---|
| Eisen (Fe) | 16000 |
| Aluminium (Al) | 13000 |
| Kalium (K) | 9200 |
| Silicium (Si) | 1500 |

### trace elements

| **Parameter** | **Results ppm** |
|---|---|
| Calcium (Ca) | 740 |
| Natrium (Na) | 710 |
| Titan (Ti) | 530 |
| Phosphor (P) | 500 |
| Strontium (Sr) | 290 |
| Wolfram (W) | 280 |
| Zink (Zn) | 280 |
| Magnesium (Mg) | 220 |
| Barium (Ba) | 150 |
| Nickel (Ni) | 140 |
| Cobalt (Co) | 130 |

# Annex XII-3 : Composition of manganese dioxide filter material “L plus” (natural ore) (German report)

**matrix** **manganese dioxide (97,5 %)**

***Main compounds***

| **Parameter** | **Results ppm** |
|---|---|
| Calcium (Ca) | 4800 |
| Schwefel (S) | 3100 |
| Eisen (Fe) | 2000 |
| Natrium (Na) | 2000 |
| Silicium (Si) | 1450 |

**Trace elements**

| **Parameter** | **Results ppm** |
|---|---|
| Kalium (K) | 700 |
| Aluminium (Al) | 520 |
| Magnesium (Mg) | 440 |
| Wolfram (W) | 230 |

# Annex XII-4 : Composition of manganese dioxide filter material ” T“ (natural ore) (German report)

Matrix manganese dioxide (97 %)

**main compounds**

| **Parameter** | **Results ppm** |
|---|---|
| Schwefel (S) | 4600 |
| Natrium (Na) | 3100 |
| Eisen (Fe) | 2600 |
| Calcium (Ca) | 320 |
| Kalium (K) | 290 |
| Magnesium (Mg) | 80 |
| Silicium (Si) | 72 |

**Traces elements**

| **Parameter** | | Results ppm |
|---|---|---|
| Silber | Ag | < 0,5 |
| Aluminium | Al | 32 |
| Gold | Au | < 1 |
| Bor | B | 4 |
| Barium | Ba | 7 |
| Beryllium | Be | 20,5 |
| Wismut | Bi | 50 |
| Cadmium | Cd | < 0,2 |
| Cer | Ce | 9 |
| Cobalt | Co | 1 |
| Chrom | Cr | 3 |
| Kupfer | Cu | 46 |

## Annex XII-5 : Composition of filter material manganese dioxide “P” (natural ore) (German report)

### Main compounds of manganese dioxide

| Parameter | Results ppm |
|---|---|
| Silicium (Si) | 244 000 |
| Mangan (Mn) | 177 000 |
| Eisen (Fe) | 48 000 |
| Calcium (Ca) | 42 400 |
| Schwefel (S) | 27 400 |
| Aluminium (Al) | 11 400 |
| Kalium (K) | 10 100 |

### Trace compounds of manganese dioxide

| Parameter | Results ppm |
|---|---|
| Barium (Ba) | 7 600 |
| Zink (Zn) | 4 300 |
| Magnesium (Mg) | 4 100 |
| Blei (Pb) | 3 400 |

### Trace compounds of manganese dioxide (cont.)

| Parameter | Results ppm |
|---|---|
| Strontium (Sr) | 540 |
| Titan (Ti) | 490 |
| Wolfram (W) | 490 |

| | |
|---|---|
| Natrium (Na) | 450 |
| Phosphor (P) | 270 |
| Vanadium (V) | 210 |
| Arsen (As) | 190 |
| Kupfer (Cu) | 160 |
| Silber (Ag) | 90 |
| Rubidium (Rb) | 88 |
| Bor (B) | 60 |
| Selen (Se) | 48 |
| Yttrium (Y) | 46 |
| Thallium (Tl) | 41 |
| Molybdän (Mo) | 37 |
| Cer (Ce) | 33 |
| Antimon (Sb) | 33 |
| Nickel (Ni) | 23 |
| Lithium (Li) | 23 |
| Cadmium (Cd) | 20 |
| Cobalt (Co) | 20 |
| Chrom (Cr) | 20 |
| Wismut (Bi) | 12 |
| Zirkonium (Zr) | 10 |
| Lanthan (La) | 8 |
| Zinn (Sn) | 5 |

**Traces below limit of Quantification**

| **Parameter** | **Results ppm** |
|---|---|
| Niob (Nb) | <30 |
| Gold (Au) | <20 |
| Tellur (Te) | <20 |
| Germanium (Ge) | <10 |

| | |
|---|---|
| Uran (U) | <10 |
| Beryllium (Be) | <5 |
| Dysprosium (Dy) | <5 |
| Erbium (Er) | <5 |
| Europium (Eu) | <5 |
| Gallium (Ga) | <5 |
| Gadolinium (Gd) | <5 |
| Hafnium (Hf) | <5 |
| Holmium (Ho) | <5 |
| Indium (In) | <5 |
| Iridium (Ir) | <5 |
| Lutetium (Lu) | <5 |
| Osmium (Os) | <5 |
| Palladium (Pd) | <5 |
| Platin(Pt) | <5 |
| Rhenium (Re) | <5 |
| Rhodium (Rh) | <5 |
| Ruthenium (Ru) | <5 |
| Samarium (Sm) | <5 |
| Terbium (Tb) | <5 |
| Thorium (Th) | <5 |
| Thulium (Tm) | <5 |
| Ytterbium (Yb) | <5 |

# ANNEX XIII - LEACHING TESTS

## Annex XIII-1 : Leaching Test (eluate-analysis) of iron oxide GEH (German report)

Elution with synthetic water since DIN EN 12902
Method: ICP-OES since DIN EN ISO 11885

| Elements | Synthetic water after leaching ppm |
|---|---|
| V | 0,076 |
| Ba | 0,040 |
| Mn | 0,012 |
| As | <0,001 |
| Cd | <0,0005 |
| Co | <0,005 |
| Cr | <0,005 |
| Cu | <0,005 |
| Hg | <0,0002 |
| Nb | <0,005 |
| Ni | <0,005 |
| Pb | <0,005 |
| Sb | <0,001 |
| Se | <0,001 |
| Ti | <0,005 |
| Zn | <0,005 |

## Annex XIII-2 : Leaching test (eluate analysis) of Manganese dioxide (natural ore concentrated) (German report)

Elution with synthetic water according to DIN EN 12902
Method : ICP-OES since DIN EN 11885

| **Elements** | | **Synthetic water after leaching ppm** |
|---|---|---|
| | | |
| Mangan | Mn | 0,031 |
| Chrom | Cr | 0,012 |
| Nickel | Ni | 0,008 |
| Kupfer | Cu | 0,010 |
| Zink | Zn | 0,01 |
| Antimon | Sb | < 0,001 |
| Arsen | As | < 0,001 |
| Cadmium | Cd | < 0,005 |
| Blei | Pb | < 0,005 |
| Quecksilber | Hg | < 0,002 |
| Selen | Se | < 0,001 |
| Kobalt | Co | < 0,005 |
| Eisen | Fe | < 0,01 |
| Aluminium | Al | < 0,01 |
| Barium | Ba | < 0,005 |

### Annex XIII-3 : Leaching test (eluate analysis) of manganese dioxide “P” (natural ore) (German report)

Elution with synthetic water according to DIN EN 12902
method: ICP-OES DIN EN ISO 11885

| Elements | Synthetic Water after leaching ppm |
|---|---|
| P | 0,710 |
| B | 0,290 |
| Ba | 0,140 |
| Zn | 0,080 |
| Al | 0,024 |
| V | 0,010 |
| As | 0,001 |
| Sb | <0,001 |
| Cd | <0,0005 |
| Cr | <0,005 |
| Pb | <0,005 |
| Hg | <0,0002 |
| Ni | <0,005 |
| Se | <0,001 |
| Ti | <0,005 |
| W | <0,010 |
| Cu | <0,005 |
| Ag | <0,005 |
| Rb | <0,010 |
| Ti | <0,001 |
| Mo | <0,005 |
| Ce | <0,010 |
| Co | <0,005 |
| Sn | <0,001 |

## ANNEX XIV - TEST PILOT SYSTEM WITH MANGANESE DIOXIDE
(natural ore) (German report)

### Annex XIV-1 : Drinking water at pH 6.0

| lfd. Nr. | Parameter | | blank water **before** treatment | start of filtration *1) **after** treatment | end of filtration *2) **after** treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 17,6 | 19,3 | 19,2 |
| 2 | Kalium (K) | mg/l | 1,9 | 2,1 | 1,9 |
| 3 | Calcium (Ca) | mg/l | 70,9 | 66,1 | 66,8 |
| 4 | Magnesium (Mg) | mg/l | 14,0 | 13,4 | 13,0 |
| 5 | Strontium (Sr) | mg/l | 0,36 | 0,21 | 0,32 |
| 6 | Eisen (Fe) | mg/l | 0,032 | 0,013 | 0,011 |
| 7 | Mangan (Mn) | mg/l | <0,005 | 0,008 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | <0,02 | <0,02 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,8 | 1,7 | 1,8 |
| 10 | Chlorid (Cl) | mg/l | 106 | 107 | 108 |
| 11 | Sulfat ($SO_4$) | mg/l | 34 | 32 | 34 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 85 | 89 | 85 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | <0,005 | <0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,006 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | <0,005 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,074 | 0,009 | 0,011 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot system with manganese dioxide (natural ore) (German report)

## Annex XIV-2 : Drinking water at pH 6.5

| lfd. Nr. | Parameter | | blank water **before** treatment | start of filtration *1) **after** treatment | end of filtration *2) **after** treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 19,1 | 17,9 | 18,3 |
| 2 | Kalium (K) | mg/l | 2,1 | 2,0 | 2,1 |
| 3 | Calcium (Ca) | mg/l | 73,7 | 69,2 | 73,7 |
| 4 | Magnesium (Mg) | mg/l | 14,0 | 14,1 | 14,1 |
| 5 | Strontium (Sr) | mg/l | 0,37 | 0,20 | 0,35 |
| 6 | Eisen (Fe) | mg/l | 0,045 | 0,025 | 0,017 |
| 7 | Mangan (Mn) | mg/l | <0,005 | <0,005 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | <0,02 | <0,02 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,8 | 2,9 | 1,8 |
| 10 | Chlorid (Cl) | mg/l | 96 | 96 | 96 |
| 11 | Sulfat ($SO_4$) | mg/l | 38 | 39 | 38 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 121 | 115 | 120 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | <0,005 | <0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,017 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | <0,005 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,079 | 0,007 | 0,007 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot system with manganese dioxide (natural ore) (German report)

## Annex XIV-3 : Mineral water at pH 6,0

| lfd. Nr. | Parameter | | mineral water **before** treatment | start of filtration *1) **after** treatment | end of filtration *2) **after** treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 138 | 130 | 130 |
| 2 | Kalium (K) | mg/l | 9,1 | 8,6 | 9,2 |
| 3 | Calcium (Ca) | mg/l | 52,6 | 55,9 | 54,9 |
| 4 | Magnesium (Mg) | mg/l | 57,4 | 59,4 | 60,6 |
| 5 | Strontium (Sr) | mg/l | 0,046 | 0,11 | 0,064 |
| 6 | Eisen (Fe) | mg/l | <0,005 | 0,008 | <0,005 |
| 7 | Mangan (Mn) | mg/l | 0,031 | 0,025 | 0,006 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | <0,02 | 0,04 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,0 | 1,0 | 1,0 |
| 10 | Chlorid (Cl) | mg/l | 62 | 64 | 65 |
| 11 | Sulfat ($SO_4$) | mg/l | 52 | 51 | 52 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 663 | 665 | 664 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | 0,006 | 0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,010 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | 0,015 | <0,005 | 0,006 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,026 | 0,017 | 0,014 |

*1) after 2 bed volumes

*2) after 20 bed volumes (end of test)

## Test pilot system with manganese dioxide (natural ore) (German report)

### Annex XIV-4 : Mineral water at pH 6.5

| lfd. Nr. | Parameter | | mineral water **before** treatment | start of filtration *1) **after** treatment | end of filtration *2) **after** treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 145 | 135 | 140 |
| 2 | Kalium (K) | mg/l | 9,4 | 8,4 | 9,5 |
| 3 | Calcium (Ca) | mg/l | 52,7 | 50,8 | 52,6 |
| 4 | Magnesium (Mg) | mg/l | 57,2 | 55,7 | 57,6 |
| 5 | Strontium (Sr) | mg/l | 0,045 | 0,083 | 0,057 |
| 6 | Eisen (Fe) | mg/l | <0,005 | <0,005 | <0,005 |
| 7 | Mangan (Mn) | mg/l | 0,032 | 0,007 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | 0,02 | 0,03 | 0,03 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,0 | 1,0 | 1,0 |
| 10 | Chlorid (Cl) | mg/l | 65 | 66 | 66 |
| 11 | Sulfat ($SO_4$) | mg/l | 53 | 52 | 53 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 665 | 653 | 661 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | 0,006 | 0,006 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,010 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | 0,015 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,026 | 0,007 | 0,006 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot systems with manganese dioxide (natural ore concentrated) (German report)

### Annex XIV-5 : Drinking water at pH 6.0

| lfd. Nr. | Parameter | | blank water **before** treatment | start of *1) filtration | end of *2) filtration |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 17,6 | 20,7 | 18,5 |
| 2 | Kalium (K) | mg/l | 1,9 | 3,0 | 2,5 |
| 3 | Calcium (Ca) | mg/l | 70,9 | 62,4 | 71,3 |
| 4 | Magnesium (Mg) | mg/l | 14,0 | 15,3 | 14,8 |
| 5 | Strontium (Sr) | mg/l | 0,36 | 0,037 | 0,18 |
| 6 | Eisen (Fe) | mg/l | 0,032 | 0,012 | 0,017 |
| 7 | Mangan (Mn) | mg/l | <0,005 | <0,005 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | <0,02 | <0,02 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,8 | 1,8 | 1,8 |
| 10 | Chlorid (Cl) | mg/l | 106 | 107 | 108 |
| 11 | Sulfat ($SO_4$) | mg/l | 34 | 22 | 32 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 85 | 103 | 103 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | <0,005 | <0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,006 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | <0,005 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,074 | <0,005 | <0,005 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot systems with manganese dioxide (natural ore concentrated) (German report)

### Annex XIV- 6 : Drinking water at pH 6.5

| lfd. Nr. | Parameter | | blank water **before** treatment | start of *1) filtration | end of *2) filtration |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 19,1 | 20,6 | 19,9 |
| 2 | Kalium (K) | mg/l | 2,1 | 2,8 | 2,5 |
| 3 | Calcium (Ca) | mg/l | 73,7 | 59,5 | 75,3 |
| 4 | Magnesium (Mg) | mg/l | 14,0 | 15,4 | 15,2 |
| 5 | Strontium (Sr) | mg/l | 0,37 | 0,022 | 0,19 |
| 6 | Eisen (Fe) | mg/l | 0,045 | 0,025 | 0,014 |
| 7 | Mangan (Mn) | mg/l | <0,005 | <0,005 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | <0,02 | <0,02 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,8 | 1,8 | 1,9 |
| 10 | Chlorid (Cl) | mg/l | 96 | 96 | 97 |
| 11 | Sulfat ($SO_4$) | mg/l | 38 | 24 | 36 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 121 | 101 | 124 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | <0,005 | 0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,017 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | <0,005 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,079 | <0,005 | <0,005 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot systems with manganese dioxide (natural ore concentrated) (German report)

### Annex XIV–7 : Mineral water at pH 6.0

| lfd. Nr. | Parameter | | Mineral water before treatment | start of filtration *1) after treatment | end of filtration *2) after treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 138 | 130 | 137 |
| 2 | Kalium (K) | mg/l | 9,1 | 7,1 | 9,2 |
| 3 | Calcium (Ca) | mg/l | 52,6 | 53,6 | 55,9 |
| 4 | Magnesium (Mg) | mg/l | 57,4 | 59,4 | 59,0 |
| 5 | Strontium (Sr) | mg/l | 0,046 | 0,020 | 0,030 |
| 6 | Eisen (Fe) | mg/l | <0,005 | 0,068 | <0,005 |
| 7 | Mangan (Mn) | mg/l | 0,031 | 0,008 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | <0,02 | 0,04 | <0,02 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,0 | 1,1 | 1,1 |
| 10 | Chlorid (Cl) | mg/l | 62 | 65 | 64 |
| 11 | Sulfat ($SO_4$) | mg/l | 52 | 43 | 51 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 663 | 680 | 672 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | 0,006 | <0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,010 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | 0,015 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,026 | <0,005 | <0,005 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

## Test pilot systems with manganese dioxide (natural ore concentrated) (German report)

## Annex XIV-8 : Mineral water at pH 6.5

| lfd. Nr. | Parameter | | Mineral water before treatment | start of filtration *1) after treatment | end of filtration *2) after treatment |
|---|---|---|---|---|---|
| 1 | Natrium (Na) | mg/l | 145 | 135 | 144 |
| 2 | Kalium (K) | mg/l | 9,4 | 5,8 | 9,3 |
| 3 | Calcium (Ca) | mg/l | 52,7 | 34,9 | 52,1 |
| 4 | Magnesium (Mg) | mg/l | 57,2 | 56,8 | 60,9 |
| 5 | Strontium (Sr) | mg/l | 0,045 | 0,010 | 0,019 |
| 6 | Eisen (Fe) | mg/l | <0,005 | 0,006 | <0,005 |
| 7 | Mangan (Mn) | mg/l | 0,032 | <0,005 | <0,005 |
| 8 | Nitrit ($NO_2$) | mg/l | 0,02 | <0,02 | 0,03 |
| 9 | Nitrat ($NO_3$) | mg/l | 1,0 | 1,0 | 1,0 |
| 10 | Chlorid (Cl) | mg/l | 65 | 66 | 66 |
| 11 | Sulfat ($SO_4$) | mg/l | 53 | 45 | 52 |
| 12 | Hydrogencarbonat ($HCO_3$) | mg/l | 665 | 565 | 649 |
| 13 | Phosphor (P) | mg/l | <0,05 | <0,05 | <0,05 |
| 14 | Aluminium (Al) | mg/l | 0,006 | <0,005 | <0,005 |
| 15 | Titan (Ti) | mg/l | <0,005 | <0,005 | <0,005 |
| 16 | Zink (Zn) | mg/l | 0,010 | <0,005 | <0,005 |
| 17 | Cobalt (Co) | mg/l | <0,005 | <0,005 | <0,005 |
| 18 | Nickel (Ni) | mg/l | 0,015 | <0,005 | <0,005 |
| 19 | Wolfram (W) | mg/l | <0,005 | <0,005 | <0,005 |
| 20 | Barium (Ba) | mg/l | 0,026 | <0,005 | <0,005 |

*1) after 2 bed volumes
*2) after 20 bed volumes (end of test)

# ANNEX XV - OXIDATION POTENTIAL

## Annex XV- 1 : Oxidation Potential Manganese Dioxide Filter Systems (German report)

| | | | **Oxidation potential** | | **By-products** | | **By-products** | **By-products** | **By-products** |
|---|---|---|---|---|---|---|---|---|---|
| **Mineral waters**<br>**5 types** | **before** | **after** | **Redox potential** | **Bromide (Br)** | **Bromate ($BrO_3$)** | **Iodide (I)** | **Iodate ($IO_3$)** | **Formaldehyde** | **THM *** |
| | | | **mV** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **µg/l** | **µg/l** |
| 1 | X | | 409 | 0.15 | <0.001 | 0.011 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 406 | 0.15 | <0.001 | 0.012 | <0.001 | <5 | <0.1/<0.5 |
| 2 | X | | 400 | 0.05 | <0.001 | 0.008 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 401 | 0.05 | <0.001 | 0.009 | <0.001 | <5 | <0.1/<0.5 |
| 3 | X | | 81 | <0.05 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| | | X F1 | 245 | <0.05 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| | | X F2 | 235 | <0.05 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| 4 | X | | 250 | <0.05 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 250 | <0.05 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| 5 | X | | 360 | 0.05 | <0.001 | <0.005 | | | <0.2/<0.5 |
| | | X | 357 | 0.08 | <0.001 | <0.005 | | | <0.2/<0.5 |

* THM limits of detection:

| | |
|---|---|
| Trichloromethane | 0.5 µg/l |
| Bromodichloromethane | 0.1/0.2 µg/l |
| Dibromochloromethane | 0.1/0.2 µg/l |
| Tribromomethane | 0.1/0.2 µg/l |

F1= filter 1
F2= filter 2

### Annex XV-2 : Oxidation Potential Iron Dioxide Filter Systems (German report)

| | | | **Oxidation potential** | | **By-products** | | **By-products** | **By-products** | **By-products** |
|---|---|---|---|---|---|---|---|---|---|
| **Mineral waters 5 types** | **before** | **after** | **Redox potential** | **Bromide (Br)** | **Bromate ($BrO_3$)** | **Iodide (I)** | **Iodate ($IO_3$)** | **Formaldehyde** | **THM *** |
| **type** | | | **mV** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **µg/l** | **µg/l** |
| 1 | X | | 225 | 0.05 | <0.001 | <0.005 | <0.005 | <5 | <0.1/<0.5 |
| | | X | 225 | 0.06 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| 2 | X | | 260 | 1.8 | <0.001 | 0.019 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 270 | 1.8 | <0.001 | 0.019 | <0.001 | <5 | <0.1/<0.5 |
| 3 | X | | 220 | 0.17 | <0.001 | 0.006 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 220 | 0.17 | <0.001 | 0.006 | <0.001 | <5 | <0.1/<0.5 |
| 4 | X | | 390 | 0.06 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| | | X F1 | 408 | 0.05 | - | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| | | X F2 | 401 | 0.06 | <0.001 | <0.005 | <0.001 | <5 | <0.1/<0.5 |
| 5 | X | | 250 | 0.32 | <0.001 | 0.007 | <0.001 | <5 | <0.1/<0.5 |
| | | X | 255 | 0.30 | <0.001 | 0.007 | <0.001 | <5 | <0.1/<0.5 |

* THM limits of detection:

| | |
|---|---|
| Trichloromethane | 0.5 µg/l |
| Bromodichloromethane | 0.1/0.2 µg/l |
| Dibromochloromethane | 0.1/0.2 µg/l |
| Tribromomethane | 0.1/0.2 µg/l |

## ANNEX XVI - IMPACT OF TREATMENT ON CHEMICAL COMPOSITION OF NMW

### Annex XVI-I : Typical results for removal arsenic with iron oxide filtration (GEH– material) (German report)

**Sampling for analysis made during process for production (no regeneration)**

| **Results** | | | |
|---|---|---|---|
| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
| pH-value | | 7,48 | 7,51 |
| Conductivity (25°C) | µS/cm | 460 | 467 |
| | | | |
| **Kations** | | | |
| Lithium (Li) | mg/l | 0,048 | 0,051 |
| Natrium (Na) | mg/l | 16,8 | 16,7 |
| Kalium (K) | mg/l | 3,2 | 3,2 |
| Ammonium ($NH_4$) | mg/l | < 0,02 | < 0,02 |
| Magnesium (Mg) | mg/l | 19,4 | 19,3 |
| Calcium (Ca) | mg/l | 54,8 | 54,5 |
| Strontium (Sr) | mg/l | 1,1 | 1,1 |
| Mangan (Mn) | mg/l | < 0,002 | < 0,002 |
| Eisen (Fe) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Anions** | | | |
| Fluorid (F) | mg/l | 0,27 | 0,27 |
| Iodid (I) | mg/l | < 0,005 | < 0,005 |
| Bromid (Br) | mg/l | 0,08 | 0,09 |
| Chlorid (Cl) | mg/l | 17,4 | 18,0 |
| Nitrit ($NO_2$) | mg/l | < 0,005 | < 0,005 |
| Nitrat ($NO_3$) | mg/l | < 0,3 | < 0,3 |
| Sulfat ($SO_4$) | mg/l | 18 | 18 |
| Hydrogenphosphat ($HPO_4$) | mg/l | < 0,04 | < 0,04 |
| Hydrogencarbonat ($HCO_3$) | mg/l | 263 | 263 |
| Carbonat ($CO_3$) | mg/l | < 3 | < 3 |
| Hydrogensulfid (HS) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Undissociated substances** | | | |
| Kieselsäure ($H_2SiO_3$) | mg/l | 18,3 | 17,8 |
| Borsäure ($HBO_2$) | mg/l | 0,16 | 0,12 |

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| **Parameter** | **Unit** | **Results<br>before treatment** | **Results<br>after treatment** |
|---|---|---|---|
| Total dissolved minerals | mg/l | 413 | 412 |
| | | | |
| **Dissolved gases** | | | |
| | | | |
| Kohlenstoffdioxid (CO2) | mg/l | 18 | 18 |
| | | | |
| **Evaporation residues** | | | |
| | | | |
| Abdampfrückstand bei 180°C | mg/l | 240 | 242 |
| Abdampfrückstand bei 260°C | mg/l | 222 | 208 |
| | | | |
| **Inorganic Compounds** | | | |
| | | | |
| Aluminium(Al) | mg/l | < 0,005 | < 0,005 |
| Arsen (As) | mg/l | 0,026 | < 0,001 |
| Antimon (Sb) | mg/l | < 0,001 | < 0,001 |
| Barium (Ba) | mg/l | 0,089 | 0,086 |
| Beryllium (Be) | mg/l | < 0,0005 | < 0,0005 |
| Blei (Pb) | mg/l | < 0,0005 | < 0,0005 |
| Bor (B) | mg/l | 0,04 | 0,03 |
| Cadmiun (Cd) | mg/l | < 0,0002 | < 0,0002 |
| Cäsium (Cs) | mg/l | < 0,005 | < 0,005 |
| Chrom (Cr) | mg/l | < 0,001 | < 0,001 |
| Kobalt (Co) | mg/l | < 0,001 | < 0,001 |
| Kupfer (Cu) | mg/l | < 0,001 | < 0,001 |
| Molybdän (Mo) | mg/l | 0,011 | 0,011 |
| Nickel (Ni) | mg/l | < 0,001 | < 0,001 |
| Quecksilber (Hg) | mg/l | < 0,0001 | < 0,0001 |
| Rubidium (Rb) | mg/l | 0,011 | 0,011 |
| Selen (Se) | mg/l | < 0,001 | < 0,001 |
| Silber (Ag) | mg/l | < 0,0005 | < 0,0005 |
| Thallium (Tl) | mg/l | < 0,0002 | < 0,0002 |
| Titan (Ti) | mg/l | < 0,001 | < 0,001 |
| Uran (U) | mg/l | 0,0009 | 0,0005 |

| | | | |
|---|---|---|---|
| Vanadium (V) | mg/l | < 0,001 | < 0,001 |
| Zink (Zn) | mg/l | < 0,005 | < 0,005 |
| Zinn (Sn) | mg/l | < 0,001 | < 0,001 |
| Sulfid (S) | mg/l | < 0,005 | < 0,005 |

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| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
|---|---|---|---|
| **Group Parameter** | | | |
| | | | |
| Spectral Absorption at 254 nm | 1/m | 0,18 | 0,15 |
| Spectral Absorption at 436 nm | 1/m | < 0,05 | < 0,05 |
| TOC | mg/l | 0,4 | 0,3 |
| Kohlenwasserstoffe nach H18 | mg/l | < 0,1 | < 0,1 |
| Cyanide (CN) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Polycyclic aromatic hydrocarbons** | | | |
| | | | |
| Fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(b)fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(k)fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(a)pyren | µg/l | < 0,002 | < 0,002 |
| Benzo(g,h,i)perylen | µg/l | < 0,002 | < 0,002 |
| Indeno(1,2,3-c,d)pyren | µg/l | < 0,002 | < 0,002 |
| | | | |
| **Solvents** | | | |
| | | | |
| Dichlormethan | µg/l | < 5 | < 5 |
| 1,1,1-Trichlorethan | µg/l | < 0,1 | < 0,1 |
| Trichlorethen | µg/l | < 0,1 | < 0,1 |
| Tetrachlorethen | µg/l | < 0,1 | < 0,1 |
| Tetrachlormethan | µg/l | < 0,1 | < 0,1 |
| | | | |
| **Trihalomethanes (Haloforms)** | | | |
| | | | |
| Trichlormethan | µg/l | < 0,5 | < 0,5 |
| Bromdichlormethan | µg/l | < 0,1 | < 0,1 |
| Dibromchlormethane | µg/l | < 0,1 | < 0,1 |

| | | | |
|---|---|---|---|
| Tribrommethan | µg/l | < 0,1 | < 0,1 |
| Summe der Trihalogenmethane | µg/l | - | |
| | | | |
| **Chlorinated Organic Compounds** | | | |
| | | | |
| cis-1,2-Dichlorethen | µg/l | < 5 | < 5 |
| Trans-1,2-Dichlorethen | µg/l | < 5 | < 5 |
| 1,1,2-Trichlorethan | µg/l | < 5 | < 5 |
| 1,2-Dichlorpropan | µg/l | < 5 | < 5 |

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| **Parameter** | **Unit** | **Results <u>before</u> treatment** | **Results <u>after</u> treatment** |
|---|---|---|---|
| 1,3-Dichlorpropan | µg/l | < 5 | < 5 |
| | | | |
| **Phenoles detected by GC** | | | |
| | | | |
| 2-Chlorphenol | µg/l | < 0,1 | < 0,1 |
| 4-Chlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,4-Dichlorphenol | µg/l | < 0,1 | < 0,1 |
| 3,5-Dichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,5-Trichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,4,6-Trichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,4,6-Tetrachlorphenol | µg/l | < 0,1 | < 0,1 |
| 4-Chlor-3-methylphenol | µg/l | < 0,5 | < 0,5 |
| Pentachlorphenol | µg/l | < 0,1 | < 0,1 |
| Phenol | µg/l | < 0,5 | < 0,5 |
| 2-Methylphenol | µg/l | < 0,1 | < 0,1 |
| 3-Methylphenol | µg/l | < 0,1 | < 0,1 |
| 4- Methylphenol | µg/l | < 0,1 | < 0,1 |
| 2,4-Dimethylphenol | µg/l | < 0,1 | < 0,1 |
| 3,4-Dimethylphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,5-Trimethylphenol | µg/l | < 0,1 | < 0,1 |
| o-Phenylphenol | µg/l | < 0,5 | < 0,5 |
| | | | |
| **Aromatic Hydrocarbons** | | | |
| Benzol | µg/l | < 1 | < 1 |

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## Annex XVI-2: Typical results for removal manganese with manganese dioxide filtration (material "L plus") (German report)

**Sampling for analysis made during process for production (after oxidant treatment)**

| **Results** | | | |
|---|---|---|---|
| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
| pH-value | | 6,03 | 6,05 |
| Conductivity (25°C) | µS/cm | 1990 | 2000 |
| | | | |
| **Kations** | | | |
| | | | |
| Lithium (Li) | mg/l | 0,48 | 0,47 |
| Natrium (Na) | mg/l | 280 | 280 |
| Kalium (K) | mg/l | 14,0 | 13,9 |
| Ammonium ($NH_4$) | mg/l | 0,83 | 0,83 |
| Magnesium (Mg) | mg/l | 38,7 | 39,0 |
| Calcium (Ca) | mg/l | 109 | 109 |
| Strontium (Sr) | mg/l | 0,30 | 0,30 |
| Mangan (Mn) | mg/l | 0,42 | 0,004 |
| Eisen (Fe) | mg/l | 0,061 | < 0,005 |
| | | | |
| **Anions** | | | |
| | | | |
| Fluorid (F) | mg/l | 0,89 | 0,88 |
| Iodid (I) | mg/l | 0,008 | 0,007 |
| Bromid (Br) | mg/l | 0,25 | 0,23 |
| Chlorid (Cl) | mg/l | 270 | 271 |
| Nitrit ($NO_2$) | mg/l | < 0,005 | < 0,005 |
| Nitrat ($NO_3$) | mg/l | < 0,3 | < 0,3 |
| Sulfat ($SO_4$) | mg/l | 16 | 16 |
| Hydrogenphosphat ($HPO_4$) | mg/l | < 0,04 | < 0,04 |
| Hydrogencarbonat ($HCO_3$) | mg/l | 810 | 815 |
| Carbonat ($CO_3$) | mg/l | < 3 | < 3 |
| Hydrogensulfid (HS) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Undissociated** | | | |

| **substances** | | | |
|---|---|---|---|
| | | | |
| Kieselsäure ($H_2SiO_3$) | mg/l | 22,2 | 22,2 |
| Borsäure ($HBO_2$) | mg/l | 1,01 | 1,01 |
| Bromat ($BrO_3$) | mg/l | < 0,001 | < 0,001 |

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| **Parameter** | **Unit** | **Results before treatment** | **Results after treatment** |
|---|---|---|---|
| | | | |
| Total dissolved minerals | mg/l | 1560 | 1570 |
| | | | |
| **Dissolved gases** | | | |
| | | | |
| Kohlenstoffdioxid (CO2) | mg/l | 1010 | 1050 |
| | | | |
| **Evaporation residues** | | | |
| | | | |
| Abdampfrückstand bei 180°C | mg/l | 1070 | 1090 |
| Abdampfrückstand bei 260°C | mg/l | 1030 | 1070 |
| | | | |
| **Inorganic Compounds** | | | |
| | | | |
| Aluminium(Al) | mg/l | < 0,005 | < 0,005 |
| Arsen (As) | mg/l | < 0,001 | < 0,001 |
| Antimon (Sb) | mg/l | < 0,001 | < 0,001 |
| Barium (Ba) | mg/l | 0,14 | 0,11 |
| Beryllium (Be) | mg/l | < 0,0005 | < 0,0005 |
| Blei (Pb) | mg/l | < 0,0005 | < 0,0005 |
| Bor (B) | mg/l | 0,25 | 0,25 |
| Cadmiun (Cd) | mg/l | < 0,0002 | < 0,0002 |
| Cäsium (Cs) | mg/l | < 0,025 | < 0,024 |
| Chrom (Cr) | mg/l | < 0,001 | < 0,001 |
| Kobalt (Co) | mg/l | < 0,001 | < 0,001 |
| Kupfer (Cu) | mg/l | < 0,001 | < 0,001 |
| Molybdän (Mo) | mg/l | < 0,001 | < 0,001 |
| Nickel (Ni) | mg/l | 0,002 | 0,001 |
| Quecksilber (Hg) | mg/l | < 0,0001 | < 0,0001 |

| | | | |
|---|---|---|---|
| Rubidium (Rb) | mg/l | 0,054 | 0,053 |
| Selen (Se) | mg/l | < 0,001 | < 0,001 |
| Silber (Ag) | mg/l | < 0,0005 | < 0,0005 |
| Thallium (Tl) | mg/l | < 0,0002 | < 0,0002 |
| Titan (Ti) | mg/l | < 0,001 | < 0,001 |
| Uran (U) | mg/l | < 0,0002 | < 0,0002 |
| Vanadium (V) | mg/l | 0,001 | 0,001 |
| Zink (Zn) | mg/l | 0,011 | 0,010 |
| Zinn (Sn) | mg/l | < 0,001 | < 0,001 |
| Sulfid (S) | mg/l | < 0,005 | < 0,005 |

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| **Parameter** | **Unit** | **Results before treatment** | **Resuls after treatment** |
|---|---|---|---|
| **Group Parameter** | | | |
| | | | |
| Spectral Absorption at 254 nm | 1/m | 0,60 | 0,30 |
| Spectral Absorption at 436 nm | 1/m | 0,13 | < 0,05 |
| TOC | mg/l | 0,5 | 0,5 |
| Kohlenwasserstoffe nach H18 | mg/l | < 0,1 | < 0,1 |
| Cyanide (CN) | mg/l | < 0,005 | < 0,005 |
| | | | |
| **Polycyclic aromatic hydrocarbons** | | | |
| | | | |
| Fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(b)fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(k)fluoranthen | µg/l | < 0,002 | < 0,002 |
| Benzo(a)pyren | µg/l | < 0,002 | < 0,002 |
| Benzo(g,h,i)perylen | µg/l | < 0,002 | < 0,002 |
| Indeno(1,2,3-c,d)pyren | µg/l | < 0,002 | < 0,002 |
| | | | |
| **Solvents** | | | |
| | | | |
| Dichlormethan | µg/l | < 5 | < 5 |
| 1,1,1-Trichlorethan | µg/l | < 0,1 | < 0,1 |
| Trichlorethen | µg/l | < 0,1 | < 0,1 |
| Tetrachlorethen | µg/l | < 0,1 | < 0,1 |
| Tetrachlormethan | µg/l | < 0,1 | < 0,1 |

| | | | |
|---|---|---|---|
| | | | |
| **Trihalomethanes (Haloforms)** | | | |
| | | | |
| Trichlormethan | µg/l | < 0,5 | < 0,5 |
| Bromdichlormethan | µg/l | < 0,1 | < 0,1 |
| Dibromchlormethane | µg/l | < 0,1 | < 0,1 |
| Tribrommethan | µg/l | < 0,1 | < 0,1 |
| Summe der Trihalogenmethane | µg/l | - | |
| | | | |
| **Chlorinated Organic Compounds** | | | |
| | | | |
| cis-1,2-Dichlorethen | µg/l | < 5 | < 5 |
| Trans-1,2-Dichlorethen | µg/l | < 5 | < 5 |
| 1,1,2-Trichlorethan | µg/l | < 5 | < 5 |
| 1,2-Dichlorpropan | µg/l | < 5 | < 5 |

| **Parameter** | **Unit** | **Results before treatment** | **Resuls after treatment** |
|---|---|---|---|
| 1,3-Dichlorpropan | µg/l | < 5 | < 5 |
| | | | |
| **Phenoles detected by GC** | | | |
| | | | |
| 2-Chlorphenol | µg/l | < 0,1 | < 0,1 |
| 4-Chlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,4-Dichlorphenol | µg/l | < 0,1 | < 0,1 |
| 3,5-Dichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,5-Trichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,4,6-Trichlorphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,4,6-Tetrachlorphenol | µg/l | < 0,1 | < 0,1 |
| 4-Chlor-3-methylphenol | µg/l | < 0,5 | < 0,5 |
| Pentachlorphenol | µg/l | < 0,1 | < 0,1 |
| Phenol | µg/l | < 0,5 | < 0,5 |
| 2-Methylphenol | µg/l | < 0,1 | < 0,1 |
| 3-Methylphenol | µg/l | < 0,1 | < 0,1 |
| 4- Methylphenol | µg/l | < 0,1 | < 0,1 |
| 2,4-Dimethylphenol | µg/l | < 0,1 | < 0,1 |

| | | | |
|---|---|---|---|
| 3,4-Dimethylphenol | µg/l | < 0,1 | < 0,1 |
| 2,3,5-Trimethylphenol | µg/l | < 0,1 | < 0,1 |
| o-Phenylphenol | µg/l | < 0,5 | < 0,5 |
| | | | |
| **Aromatic Hyrocarbon** | | | |
| | | | |
| Benzol | µg/l | < 1 | < 1 |
| Formaldehyd | µg/l | < 5 | < 5 |
| | | | |
| **Radionuclides** | | | |
| | | | |
| Radon-222 | Bq/l | 17 | 18 |
| Radium-226 | mBq/l | 55 | 27 |
| Radium-228 | mBq/l | 38 | 21 |

## ANNEX XVII - BY-PRODUCTS (German report)

**Analytic of by-products in the first step water after initialisation by ozone of manganese dioxide filter systems**

| | **Bromate ($BrO_3$)** | **THM *** |
|---|---|---|
| | **mg/l** | **µg/l** |
| Test 1 | <0.001 | <0.2/<0.5 |
| Test 2 | <0.001 | <0.2/<0.5 |

* THM limits of detection:

| | |
|---|---|
| Trichloromethane | 0.5 µg/l |
| Bromodichloromethane | 0.2 µg/l |
| Dibromochloromethane | 0.2 µg/l |
| Tribromomethane | 0.2 µg/l |

## ANNEX XVIII - MONITORING AND CONTROL

Besides traditional laboratory measurements to check the quality of the filtered product, the plan also prescribes the following rules, in cumulative order:

- *Before adding the capture medium:*
  - Check that the medium will perform the desired role and that its interaction with the water to be treated will not alter either the medium or the filtered water.

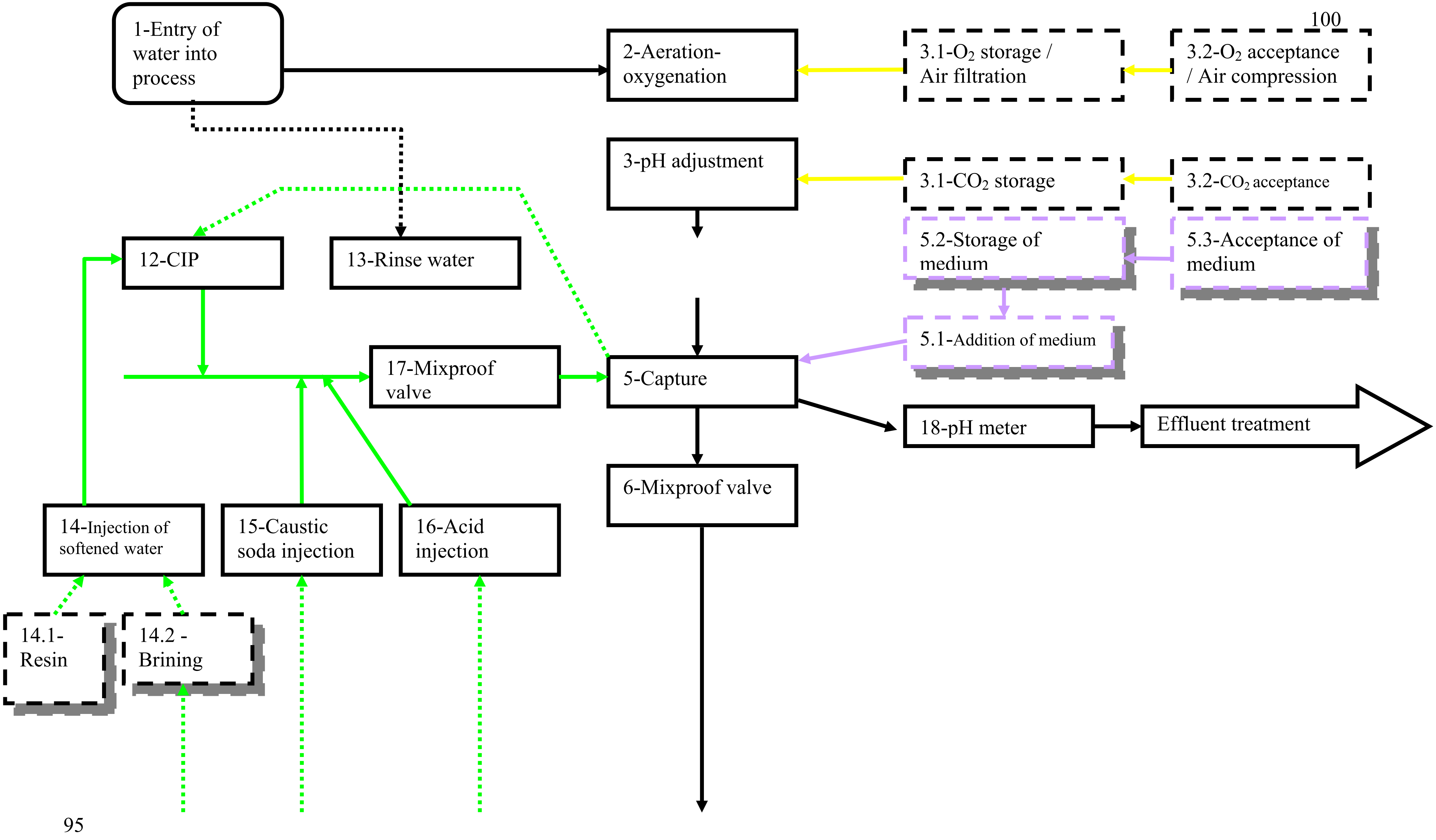
- *During production:*
  - A pH meter warns of a drift outside the medium's stability zone if this zone is narrow and depends on various interventions.
  - An oximeter ensures that the medium is keeping the undesirable element in the capture zone if this zone is narrow and depends on various interventions.

- *During regeneration:*
  - The pH meter ensures that there is no regenerant residue in the filtered water following the installation of a regenerated filter.
  - A series of analyses including pH, conductivity, bicarbonates and others selected by the operator according to the water and the regeneration products, to constitute an integrity test ensuring that the composition of the water is recovered after filtering with a regenerated filter. If positive, this test enables the quality department to authorise the re-installation of a filter in the capture system.

Depending on the medium and the water characteristics, some processes will be very sound, as they will be well within the stability domain of the minerals comprising the added or self-generated media. For these processes, traditional laboratory measurements will suffice to monitor the quality.

More delicate waters, particularly with slightly acidic pHs, will require more interventions to accelerate gas exchanges similar to those that occur naturally during transportation, simple iron removal or conditioning in bottles. When such waters are involved, the medium's properties will need to be checked and specific probes used to ensure that the operating conditions are as intended.

Finally, if the capture capacity becomes exhausted, the operator must choose between regeneration and replacement, depending on the cost of the medium and the ease with which regeneration can take place. If he opts for replacement, he should not include additional control points that apply only to regeneration.


100
1-Entry of water into process
2-Aeration-oxygenation
3.1-O₂ storage / Air filtration
3.2-O₂ acceptance / Air compression
3-pH adjustment
3.1-CO₂ storage
3.2-CO₂ acceptance
5.2-Storage of medium
5.3-Acceptance of medium
5.1-Addition of medium
12-CIP
13-Rinse water
17-Mixproof valve
5-Capture
18-pH meter
Effluent treatment
6-Mixproof valve
14-Injection of softened water
15-Caustic soda injection
16-Acid injection
14.1-Resin
14.2 -Brining
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