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LICENTIATE THESIS

Treatment of Acidic Ground Water Containing Iron and Manganese

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PREFACE

This licentiate thesis is the result of a research project carried out in 1991-1995 at the Department of Sanitary Engineering, Chalmers University of Technology, Göteborg. It is a subproject to the project ”Actions Against Acidic Well Water” initiated and financed by the National Swedish Food Administration and by the Geological Survey of Sweden.

The aim of the project ”Actions Against Acidic Well Water” was to support research, carry out investigations, improve knowledge and inform the public about technical solutions for acidic well water.

The overall objective of this project was to obtain a better understanding of the reaction mechanism and properties of filter materials for the neutralisation of acidic well water in order to mitigate pipe corrosion and to study suitable filter materials for the removal of iron and manganese from acidic well water.

This project was divided into four parts:

- A literature review of calcium carbonate dissolution and existing neutralisation units.
- An investigation of filter materials for the neutralisation of acidic water in private water supply wells in order to obtain better understanding of their reaction with acidic water.
- A literature review of existing methods for the removal of soluble iron and manganese in ground water, focused on methods that can be applied in small systems. The fundamental environmental chemistry of iron and manganese was also described.
- An investigation of filter materials for the neutralisation of acidic water in private water supply wells in order to obtain better understanding of their reaction with acidic water containing iron and manganese. Catalytic filter materials for the removal of iron and manganese in ground water were also examined.

I would like to thank all people who have been involved and helped me in different ways during my work on this project. I especially want to thank: my supervisor professor Torsten Hedberg for his advice, discussions and support; Evy Axén for helping with laboratory analyses and Lena Björklund for helping with the experimental work in the last part of the project.

Göteborg, February 1997

Gittan Horkeby

ABSTRACT

Ground water in private wells, in Sweden, is often acidic with concentrations of iron and manganese exceeding drinking water standards. To increase pH and decrease the concentrations of iron and manganese, different filter materials suitable for the treatment of water from private water supply wells, exist.

At the Department of Sanitary Engineering, Chalmers University of Technology, Göteborg, Sweden, calcareous filter materials (limestone and semicalcined dolomite) for the neutralisation and catalytic filter materials for the removal of iron and manganese have been investigated in pilot columns. During the examination, water quality including pH, alkalinity, total hardness, iron, manganese and organic material have been varied. Besides that, the particle size of the filter material, depth of contact and fluid velocity were varied. The effect of back-washing was investigated. To explain the removal mechanism for iron and manganese in calcareous materials, the porosity of the materials was analysed.

A literature review concerning dissolution of calcareous filter materials and existing methods for the removal of iron and manganese was carried out.

The results show that limestone is suitable for treating very soft acidic water with low concentrations of carbon dioxide to reach the pH to 7.5-9.0, recommended by the Swedish Food Administration. When treating medium hard water with a relatively high concentration of carbon dioxide, a semicalcined dolomite filter material is recommended. The effect of an increase in pH is dependent on the particle size of the filter material. This is most obvious for limestone, where an increase in particle size requires an increase in reaction time. The neutralisation efficiency of calcareous filter materials decreases with increasing iron and manganese concentrations in the water.

The results clearly show that iron is removed by all types of calcareous filter material, while manganese is removed only by semicalcined dolomite. The removal mechanisms in limestone and dolomite filter materials, are not the same for iron as for manganese. Iron precipitates in the bulk solution between the particles of the filter material, while manganese precipitates closer to the particle surface in the diffusion layer or is adsorbed in the pores of the granulated material. After back-washing a significant amount of metal from treated water remains in the filter bed.

Results from tests with catalytic filter materials for the removal of iron and manganese, indicated that Manganese Greensand is effective if it is regularly regenerated with potassium permanganate. Its efficiency decreases however if the influent concentration of iron is high (> 1 mg Fe/l). Another catalytic filter material, Birm, is also negatively affected by high concentrations of iron in the water as well as organic material.

Keywords: Acidic ground water, private wells, alkalisation, neutralisation, iron, manganese, filter material, calcareous, limestone, semicalcined dolomite, catalytic material, Manganese Greensand, Birm, Manganese Dioxide

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Horkeby, G. (1992) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Publ. 1:92. 156 pp.

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IV Filter Materials for the Treatment of Acidic Well Water Containing Iron and Manganese - an Investigation of their Properties (Filtermassor för behandling av sura, järn- och manganhaltiga brunnsvatten - en undersökning av dess egenskaper)
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1. INTRODUCTION

1.1 Background

Environmental acidification has influenced the water quality in lakes, rivers and ground water. The SO_2 and NO_x emissions from power stations on the European continent are the main reasons for the formation of acid rain.

Many lakes and rivers in Sweden located on low weathering bedrock or surrounded by soils with a low calcite content, are suffering from the effects of acid rain.

The general appearance of acidic ground water, caused by acid rain, is mainly dependent of the weathering resistance and low content of calcite in the soils and rocks as well as coarse materials of the aquifers. This acidification caused by sulphur and nitrogen deposition decreases the alkalinity and pH, and increases the sulphate concentration in the ground water.

Besides the acidification caused by deposition, there is natural soil and ground water acidification caused by carbonic acid and organic acids from the decomposition of organic materials. Carbonic acid is a very weak acid and the resulting pH will be over 6. Organic acids, however, have a wide range of pK_a values.

Acidic ground water in many private wells often leads to corrosion of the plumbing system in buildings and this leads to increased concentrations of copper and iron in the water. The main problems are technical and aesthetic, but high concentrations of copper can affect health, especially concerning small children. To mitigate these problems the water can be treated in filter units containing calcareous (limestone or dolomite) materials, also referred to as neutralisation materials, in order to increase pH and alkalinity.

It has long been accepted that the alkalinity in combination with the calcium concentration in the water, is important for iron pipe corrosion (Langelier 1936). If the equilibrium point for precipitation of calcium carbonate is exceeded, due to increased pH or alkalinity, a calcium carbonate layer is formed inside the pipe. This layer was considered to prevent corrosion, but recent corrosion research has shown that it is more complicated.

Corrosion of copper is common at low pH or in hard water. Investigations have shown that increased alkalinity does not have the same preventive effect for copper as for iron corrosion (Enander & Berghult 1994, Lind Johansson *et al* 1994, Sander *et al* 1996). The internal corrosion of copper pipes increased with increasing concentration of carbon dioxide in the water. If the equilibrium point for calcium carbonate is exceeded, precipitation is obtained as well as decreasing pH and increasing concentration of carbon dioxide. This leads to increased copper corrosion.

In order to prevent corrosion of copper pipes, the concentration of calcium should be low and pH high. In high alkalinity water, a high pH is very important in order to have a low carbon dioxide concentration.

In order to reduce corrosion problems, limits and recommendations were set by the National Swedish Food Administration (1989) for drinking water from private wells and treatment plants, Table 1.1 shows guidelines for pH, alkalinity and total hardness in water for private wells (National Swedish Food Administration 1989 and 1993).

Another common problem in private wells is when the concentration of iron and manganese in the ground water exceeds drinking water standards. This in turn will cause taste, staining and discoloration of clothes and sanitary ware, as well as precipitates which reduce pipe diameters and clog valves. There are no direct negative effects on health caused by iron and manganese in drinking water, the problems are technical and aesthetic. Table 1.1 shows maximum concentration of iron and manganese in water from private wells, recommended by the National Swedish Food Administration (1989) and (1993).

There are many methods published in literature concerning the removal of iron and manganese in water treatment plants, but there is a lack of publications about the treatment in small private systems. However, one frequently used method for removal of iron and manganese in private water supplies is to filter the water through catalytic filter materials.

Table 1.1 Directives for water quality. (National Swedish Food Administration 1989). The same directives were recommended in 1993.

Parameter	Parametric value
pH	7.5-9.0
Alkalinity mg HCO_3^-/l	> 60
Calcium mg Ca^{2+}/l	20-60
Iron mg Fe/l	< 0.5
Manganese mg Mn/l	< 0.3

1.2 Aims of the project

The objectives of this study are:

- to perform a literature review of existing methods for the controlling of pH and the removal of soluble iron and manganese in ground water.

- to perform an investigation of filter materials for the neutralisation of acidic water in private water supply wells in order to obtain a better understanding of their reaction with acidic water and their ability to reach the pH to 7.5 - 9.0, recommended by the National Swedish Food Administration.

- to perform an investigation of filter materials used for the removal of iron and manganese in order to give guidelines and recommendations for the treatment of acidic ground water containing iron and manganese, from private water supply wells.

1.3 The scope of the project

This licentiate thesis is based on the work contained in the following publications.

I Filter Materials for the Neutralisation - an Investigation of their Properties for the Treatment of Acidic Well Water (Filtermassor för avsyrning - en undersökning av dess egenskaper för behandling av sura brunnsvatten)
Horkeby, G. (1992) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Publ. 1:92.

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Horkeby, G., Björklund, L. (1995) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Report 1995:2

V Water Treatment Handbook for Acidic Well Water Containing Iron and Manganese (Handbok för behandling av sura järn- och manganhaltiga brunnsvatten)
Horkeby, G. (1995) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Report 1995:3

2. TREATMENT PROCESSES FOR ACIDIC WATER CONTAINING IRON AND MANGANESE

In this chapter, different processes for the treatment of acidic ground water containing iron and manganese are described.

Removal of iron and manganese from ground water and controlling the pH can be performed in different ways. The appropriate process depends on water quality and the size of system (Horkeby 1992, 1993). In table 2.1 different methods are listed and some of them are suitable for small systems.

Table 2.1. Methods for the treatment of acidic water, containing iron and manganese.

Process	Method
Alkalisation	Aeration Chemical addition Filtration through calcareous materials
Oxidation by aeration	Aeration + sand filtration Aeration + sedimentation + sand filtration Aeration + pH adjustment + sand filtration
Oxidants addition	Chlorine, chlorine dioxide, hypochlorites + filtration Potassiumpermanganate + filtration Oxidation by ozone + filtration Hydrogen peroxide + filtration
Catalytic oxidation	Filtration through Manganese Greeensand Filtration through Birm Filtration through Manganese Dioxide
Flocculation	Al- or Fe-salt + flocculation + filtration
Softening process	Coprecipitation
Adsorption	Activated carbon Calcareous materials
Membrane filtration	Ultrafiltration Nanofiltration Reverse osmosis
Ion exchange	Cation resin Anion resin
Other processes	Well construction Oxidation in the ground Biological treatment

2.1 Alkalisation

2.1.1 Aeration

Aeration is a method by which water and air are brought into close contact to remove excessive carbon dioxide. Tillmans (1912) set up equations which determine whether a given water is undersaturated, well balanced or oversaturated, with regard to free dissolved CO_2. Figure 2.1 shows the different forms of CO_2 in water (Tillmans 1912).

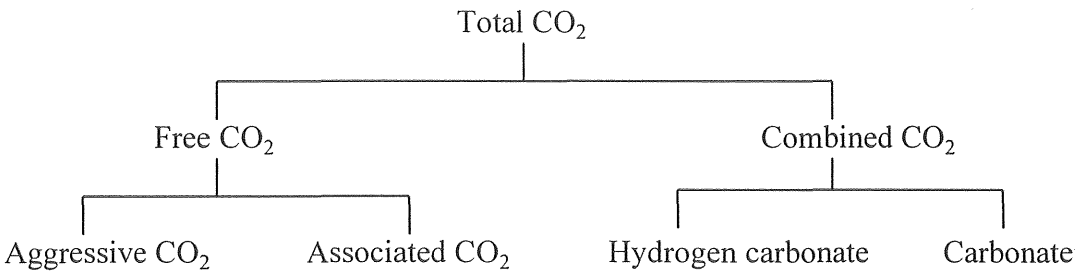

Figure 2.1. Distribution of CO_2 in water.

To maintain calcium carbonate in solution, a quantity of free CO_2, known as equilibrium CO_2 or associated CO_2 is required.

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (2\text{-}1)$$

In practice the removal of excessive CO_2 will only go as far as 5-10 mg CO_2/l.

2.1.2 Chemical addition

Adjustment of pH can be performed by chemical addition. Useful chemicals are calcium hydroxide, sodium hydroxide or sodium carbonate.

Adding $Ca(OH)_2$ for pH adjustment is not a method suitable for small systems in private households. That is because the dosing must be carefully controlled and adjusted to the composition of the given water. Too high a dose can lead to clogging, caused by precipitation of calcium carbonate. Sodium hydroxide or sodium carbonate is prefered for private water supply wells.

2.1.3 Filtration through calcareous materials

During this filtration process, the aggressive carbon dioxide forms hydrogen carbonates. Two different types of filter materials for the neutralisation of water exist, crushed limestone and semicalcined dolomite. Filter materials are available on the market, in various grain sizes, chemical composition and texture.

The engineering design of a limestone or dolomite filter unit requires an understanding of the kinetics of the neutralisation reaction.

In the literature there are a number of publications concerning the dissolution process of limestone and dolomite in acid water. These are summarised by Horkeby (1992).

2.1.3.1 Limestone

Limestone filter media consists of crushed limestone which contains about 99% calcium carbonate. The composition and properties of the material vary depending on source and formation.

During the filtration process, carbon dioxide forms hydrogen carbonate. At sufficiently long contact times, the conversion of CO_2, according to the reaction (2-2), should theoretically continue until the calcium carbonate/carbonic acid equilibrium is reached. At pH over 6 this is the dominating reaction while reaction (2-3), is predominant at pH values less than 6.

The overall neutralisation and dissolution reactions:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (2\text{-}2)$$

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \qquad (2\text{-}3)$$

Letterman has studied the dissolution reaction using through-flow packed-bed reactors (Letterman 1986, 1991, 1993). According to him, the rate of dissolution of calcium carbonate, in a packed bed with crushed limestone, is controlled by two processes that act in series - a surface reaction that controls the release of calcium from the solid and a mass transfer resistance that controls the rate of calcium transport between the solid surface and the bulk solution.

A schematic diagram illustrating the overall dissolution process is presented in figure 2.2. The net release of calcium and carbonate from the particle surface to the solution, is dependent on adsorption of H^+ or H_2O on the $CaCO_3$ surface and desorption of reaction products. This means that adsorption of H^+ on the surface and the rate of decomposition, increase with decreasing pH.

The rate of dissolution is also influenced by the superficial velocity. With increasing velocity the rate of dissolution increases because of decreasing diffusion boundary layers.

To sum up, the dissolution of calcium carbonate in a filter column depends on a number of parameters:

- The raw water quality: pH, content of carbon dioxide, concentration of calcium and temperature.
- Superficial velocity.
- If the system is undersaturated or in lime-carbon dioxide equilibrium.
- Grain size and structure of the limestone.

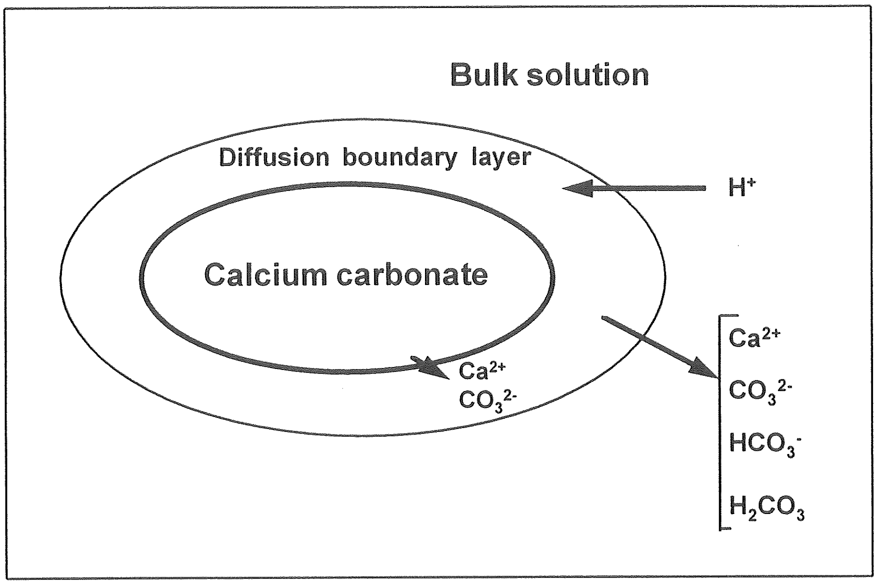

Figure 2.2. Schematic representation of the calcium carbonate dissolution process (Horkeby & Björklund 1995).

According to a literature reveiw (Horkeby 1992) the initial rate of calcite dissolution is a function of the concentration of hydrogen ions in the solution, when pH is under <5, i.e. the dissolution increases with decreasing pH. At pH over 5, the concentration of CO_2 affects the dissolution rate. However, there are different opinions about whether the rate of dissolution is controlled by diffusion or by surface reactions.

Table 2.2 shows chemical composition and grain size of some limestone filter media. It appears from the table that there is a higher content of MgO in Hydrolit Ca than in the others. Hydrolit Ca is also more porous and differs in appearance.

Table 2.2. Chemical composition and grain size for limestone filter media (based on product information)

Filter media	Grain size [mm]	$CaCO_3$ %	MgO %	Me_mO_n % *
Hydrokarbonat (Weiss, Weissjura-ε)	0.7-1.4 1.2-1.8 1.8-2.5	99.5	0.16	0.18
Filtercarb	0.8-1.2 1.2-1.8	99.2	0.22	0.39
Aqua Ring	4.0-11.0	99.76	<0.21	<0.21
Hydrolit Ca	0.5-2.5	87	4.9	1.0

* $Me_mO_n = Fe_2O_3 + Al_2O_3 + SiO_2$

2.1.3.2 Semicalcined dolomite

Semicalcined filter media is obtained through thermal processing of dolomite rock. This process generates semicalcined dolomite and gaseous CO_2, according to the reaction (2-4).

$$CaCO_3MgCO_3 \xrightarrow{700^\circ C} CaCO_3MgO + CO_2 \quad (2\text{-}4)$$

There are dolomite filter media, e.g. Akdolit Gran, which are produced through total calcining followed by hydration, granulation and recarbonisation. During the hydration process some magnesium oxide will react to form magnesium hydroxide. Some calcium hydroxide as well is formed from calcium oxide. This in turn can lead to a very high pH, upp to 12, in the water after filtration.

The dissolution reactions between water containing carbon dioxide and semicalcined dolomite, in filter beds, are described by Reijnen (1976, 1988):

$$MgO + H_2O \leftrightarrow Mg^{2+} + 2OH^- \quad (2\text{-}5)$$

$$\underline{2(OH^- + CO_2 \leftrightarrow HCO_3^-)} \quad (2\text{-}6)$$

$$MgO + H_2O + 2CO_2 \leftrightarrow Mg^{2+} + 2HCO_3^- \quad (2\text{-}7)$$

The overall deacidification reaction with MgO

$$2HCO_3^- + Ca^{2+} \leftrightarrow H_2O + CaCO_3 + CO_2 \quad (2\text{-}8)$$

$$\underline{CO_2 + OH^- \leftrightarrow HCO_3^-} \quad (2\text{-}9)$$

$$Ca^{2+} + HCO_3^- + OH^- \leftrightarrow CaCO_3 + H_2O \quad (2\text{-}10)$$

The overall reaction for $CaCO_3$ precipitation in alkaline conditions

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (2\text{-}11)$$

$$\underline{CO_3^{2-} + CO_2 + H_2O \leftrightarrow 2HCO_3^-} \quad (2\text{-}12)$$

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (2\text{-}13)$$

The overall deacidification reaction with $CaCO_3$

The dissolution of MgO, reaction (2-5), is rapid. A high concentration of Mg^{2+} and OH^- will appear in the diffusion layer around the particles and CO_2 is transformed to hydrogen carbonate (2-6). The appearance of HCO_3^- and high pH can cause precipitation of $CaCO_3$ (2-10) and blocking of the MgO crystal.

The overall rate of deacidification is given by the equation (Reijnen 1976, 1988):

$$\frac{-d[CO_2]}{dt} = k_1[CO_3^{2-}][CO_2] - k_2[HCO_3^-]^2 + k_3[OH^-][CO_2] \qquad (2\text{-}14)$$

k_1, k_2 are dissolution-rate constants, according to reaction (2-12) (k_1 in the left and k_2 in the right direction) and k_3 is the dissolution-rate constant according to reaction (2-6).

Table 2.3 shows the chemical composition and grain size for semicalcined dolomite filter media. Dolomite filter media for water treatment has to fit the standards set up in the German standard, DIN 19621. According to this, the sum of magnesium oxide and hydroxide must be at least 23% as MgO.

Table 2.3. Chemical composition and grain size for semicalcined dolomite filter media (based on product information).

Filter media	Grain size [mm]	$CaCO_3$ %	$MgO + Mg(OH)_2$ %	Me_mO_n % *
Magno Dol	0.5-2.5 2.0-4.5	73.3	26.0	0.9
Akdolit Gran	0.5-1.2 0.5-2.5 2.0-4.5 4.0-7.0	71.7	25.8	0.9
Redolit	1.0-3.0	about 70	26-28	0.5

* $Me_mO_n = Fe_2O_3 + Al_2O_3 + SiO_2$

2.2 Aeration and filtration

A frequently used process to remove iron and manganese from well water is by aeration and filtration. Oxygen from the atmosphere reacts with iron and manganese in raw water to produce relatively insoluble salts of ferric and manganic oxides. In installations of this type, oxidation may be effected by spraying the water in the air, by running the water over a contact material, with or without air circulation or, more often, by emulsion of compressed air in closed vessels.

The oxidation rate is highly dependent on pH, and increases with increasing pH. At normal pH values, oxidation of iron is rapid. In most types of ground water however, the content of dissolved carbon dioxide is high and their pH is usually <7. As water is aerated, dissolved carbon dioxide is stripped out of solution and pH increases. If pH is raised high enough, ferrous carbonate (siderite) will precipitate. The fact that ferrous carbonate can be expected to precipitate and then remain unoxidised, means that filters in iron-removal plants may be removing ferrous carbonate rather than ferric hydroxide (Olson 1975).

According to Robinson & Bredland (1968) iron removal by aeration, sedimentation and filtration is difficult to perform in ground water having natural hydrogen carbonate alkalinity of less than 50 mg/l as $CaCO_3$ (61 mg/l as HCO_3^-). Ferrous iron oxidation rates can be increased by raising the hydrogen carbonate alkalinity.

In comparison to iron, the rate of oxidation for manganese is slower in the normal pH range of natural water. Manganese is effectively oxidised when the pH is raised above 9-9.5 and when pH drops below approximately 9.0, a considerable decrease in oxidation of manganese occurs (Robinson & Bredland 1968, O' Connor 1971, Robinson & Dixon 1968). The fact that iron is easier to remove from water by aeration and filtration than manganese is mainly dependent on the difference in the standard electrode potential of both types of metals (Baozhen *et al* 1985, Stumm & Morgan 1981). The standard electron potential for oxidation of Mn^{2+} to MnO_2 is 1.29 V while the potential for oxidation of Fe^{2+} to Fe^{3+} is only 0.77 V.

The solubility of $MnCO_3$ is higher than $FeCO_3$. In attempt to remove manganese in the form of $MnCO_3$, acceptably low levels could not be achieved until the pH was greater than 9.0 (Cleasby 1975).

The aeration-filtration process is generally recommended for water with high concentrations (>5.0 mg/l) of iron (Wong 1984). For water containing manganese and organic matter other processes are recommended e.g. oxidation by chemicals.

2.3 Oxidising agents

2.3.1 Oxidation by chlorine compounds

Oxidation of iron and manganese by chlorine, hypochlorite or chlorine dioxide is described by Horkeby (1993). The method is not suitable for private water supply wells and is therefore not described here.

2.3.2 Oxidation by potassium permanganate

In water treatment plants, potassium permanganate is commonly used to oxidise iron and manganese. Potassium permanganate, is odourless, does not produce harmful vapours and can be handled safely using conventional methods. It is also a stronger oxidising agent than chlorine and chlorine compounds.

Iron oxidation by potassium permanganate is essentially instantaneous in the absence of DOC (dissolved organic carbon) and pH above 5.5. When $KMnO_4$ was added, at a dose of 105 % of the stoichiometric requirement, to a water containing 2.0 mg/l Fe(II), the iron concentration was reduced to < 0.1 mg/l after a reaction time as short as 0.1 second. (Knocke *et al* 1990).

Soluble manganese is rapidly oxidised by potassium permanganate in low DOC water over the pH range 5.5 to 9.0 (Knocke *et al* 1990).

It is convenient to oxidise iron by aeration before adding potassium permanganate to minimise the dosage. In hard alkaline water, iron is removed most effectively as $FeCO_3$, rather than $Fe(OH)_3$ and lower head losses occur in deep bed filters. Therefore chemical oxidants, when needed for manganese oxidation, should be added after the $FeCO_3$ has precipitated. Because Mn^{2+} is rapidly oxidised by chemical oxidants, the oxidants should be added just prior to filtration, allowing the MnO_2 to precipitate within the filter where it is catalysed by previous deposits of MnO_2 on the filter grain surfaces (Cleasby 1975).

2.3.3 Oxidation by ozone

Ozone is very effective in oxidising iron and manganese (Baozhen *et al* 1985), but it is not suitable for private households.

2.3.4 Oxidation by hydrogen peroxide

Knocke *et al* (1990) have examined oxidation of iron and manganese by hydrogen peroxide. However, no evidence of a reaction between Mn(II) and H_2O_2 was observed over the pH range 5.5 to 8.5. Uncomplexed Fe(II) was oxidised efficiently by H_2O_2 over the pH range 5.0 to 7.0, however not as rapidly as when using the other oxidising agents. The rate of oxidation increases with increasing pH. Complete Fe(II) oxidation was accomplished in approximately 5 seconds at pH 7.0, in comparison, nearly 3 to 5 minutes were required at pH 5.5 to achieve the same degree of oxidation. An increase in the H_2O_2 dosage likewise, yielded a significant increase in the oxidation rate. Complexed Fe(II) was however relatively stable, even in the presence of significant dosages of H_2O_2. Finally, increasing the temperature of the solution had a pronounced effect on oxidation rate.

2.4 Catalytic oxidation

Catalytic oxidation is a commonly used method for removing iron and manganese in drinking water.

Some manganese oxides have catalytic properties that can be used for catalytic oxidation. The oxidation process is an heterogeneous autocatalytical process in which a filter has to be used for the removal of manganese oxide and ferric hydroxide formed. At the same time the filter acts as a reactor in which contact between liquid and catalyst is ensured (Graveland & Heertjes 1975).

The principle for iron and manganese removal by a catalytic filter media is that of an oxidising agent added to the water to be treated. The water is then passed through a filter containing the appropriate medium. The reaction takes place rapidly at pH values as low as 6.5 with the iron and manganese being deposited on the surface of the filter media. At sufficient contact time with the catalytic medium, iron and manganese are removed and water having Fe and Mn values below guide limits is achieved. Depending upon the concentrations of iron and manganese in the raw water and the severity of the back-wash employed, the grains of filter media may increase or decrease in size (Briggs 1993, Souter 1993).

The following sections give summarised information concerning the theoretical background of catalytic oxidation and the most common filter media for iron and manganese removal. A more detailed description is given by Horkeby (1993). There are three different filter media for iron and manganese removal; Manganese Greensand, Birm and Manganese Dioxide.

2.4.1 Manganese Greensand (product name)

The most common filter media is Manganese Greensand which has been processed from a glauconitic greensand mineral. Glauconite is a silica mineral $(K,(Fe,Mg,Al)_2(Si_4O_{10})(OH)_2)$ forming small green grains in marine sedimentary minerals.

The glauconite mineral has been treated with potassium permanganate to form manganese dioxides on the surface of the grains. The treated greensand is a purple-black filter media which is capable of removing iron, manganese and hydrogen sulphide to accepted limits.

Soluble iron and manganese are oxidised and precipitated by contact with higher oxides of manganese on the greensand granules. Precipitates are then filtered and removed by back-washing. When the oxidising capacity power of the Manganese Greensand is exhausted the bed has to be regenerated with a weak potassium permanganate solution.

2.4.2 Birm (product name)

Birm is a granular filter media used for removing of iron and manganese from water supplies. It consists of a light silicon dioxide core coated with manganese dioxide, with a particle density of 1.5 g/cm^3, a bulk density of less than 0.8 kg/dm^3 and a uniform particle size. Birm is a catalyst which does not require chemicals for regeneration, but it does require an oxygen content of at least 15% of the iron and manganese content in the water as mg/l, and periodic back-washing. Birm's irregular and somewhat porous coating maximises the catalytic surface area. Birm is supplied in two grades, regular (0.61 mm) and fine (0.49 mm). The fine grade is recommended in domestic installations where back-wash rates are limited (Clack Corporation 1993, Hemp 1989).

As Birm is a catalytical media, iron and manganese will be oxidised as long as the manganese dioxide surface is in direct contact with the water. The precipitate formed is flocculated and the forces keeping the flocc in the filter are weak. It is important to back-wash the filter regularly to reduce filter head loss.

2.4.3 Manganese Dioxide (product name)

Manganese Dioxide filter medium is produced from an ore specially selected for its catalytic properties and is accurately screened to a size range of 0.355-0.850 mm. This range is chosen according to the different densities of Manganese Dioxide and silica sand. The Manganese Dioxide is placed on the surface of the sand bed and after back-washing, the two media are thoroughly mixed. It is very important that the Manganese Dioxide should mix thoroughly with the sand so that the water passing through the filter comes in contact with as much Manganese Dioxide as possible. After a period of operation, the sand grains themselves become coated with manganese oxides precipitated from the water being treated.

The water being treated should be aerated to a minimum of 60% oxygen saturation. For most applications with water having iron content up to about 1.5 mg/l and manganese content up to aproximately 0.5 mg/l, a mixed bed of 20% Manganese Dioxide and 80% sand by volume, with an empty bed residence time of 12 minutes, is found to perform satisfactorily (Briggs 1993).

2.5 Flocculation by Al- or Fe-salts

Treatment by flocculation is a commonly used method for water with iron and manganese complexed by organic material. Frequently used chemicals are aluminium sulphate or iron chloride. The process is usually only used for the treatment of surface water and is therefore not discussed here.

2.6 Removal of iron and manganese in a softening process

The softening process can be used for removing iron and manganese from water with high concentrations of free carbon dioxide and from water with high carbonate hardness. Added lime ($Ca(OH)_2$) will react with carbon dioxide and precipitate as calcium carbonate. Iron and manganese will coprecipitate as divalent hydroxides and after aerating, oxidise to $Fe(OH)_3$ and MnO_2 which are removed by filtration (Vattenteknik AB 1992, van Dijk & Wilms 1991).

2.7 Adsorption

2.7.1 Activated carbon

Activated carbon is used as a complement to other treatment methods for water with a high content of organic matter. The adsorption activity of the activated carbon depends on the raw material, method of production and particle size.

2.7.2 Calcareous filter material

The main application for calcareous filter material e.g. limestone and semicalcined dolomite (Hedberg 1983, Horkeby 1992) is for reducing the corrosive properties of acidic water, see 2.1.3. Another application is the removal of iron and manganese from water (Baldauf 1986, Beeftink 1976, Börner 1961, Hamidi & Smith 1992, Hatva *et al* 1985, Jönsson 1984, Meijers *et al* 1979, Shablovskaya *et al* 1988) which is described in Chapter 4.2.1.

2.8 Membrane processes

Membrane processes are commonly used to separate particles and dissolved substances from water. There are four different membrane processes; micro filtration, ultra filtration, nano filtration and reverse osmosis. The main difference between the processes are the size of separated particles (Baier *et al* 1987, Bersillon *et al* 1990, van Dijk & Oomen 1980, Sikora *et al* 1989, Vattenteknik AB 1992, Stenström 1995). Figure 2.3 summarises the size of water pollutants and the range of action for the different pressure driven membrane processes compared to conventional filtration processes.

The ultra filtration process could be used for the treatment of water containing iron complexed to organic material (Bersillon *et al* 1989). Using reverse osmosis an amount of 99% of ionised forms of iron and manganese can be removed.

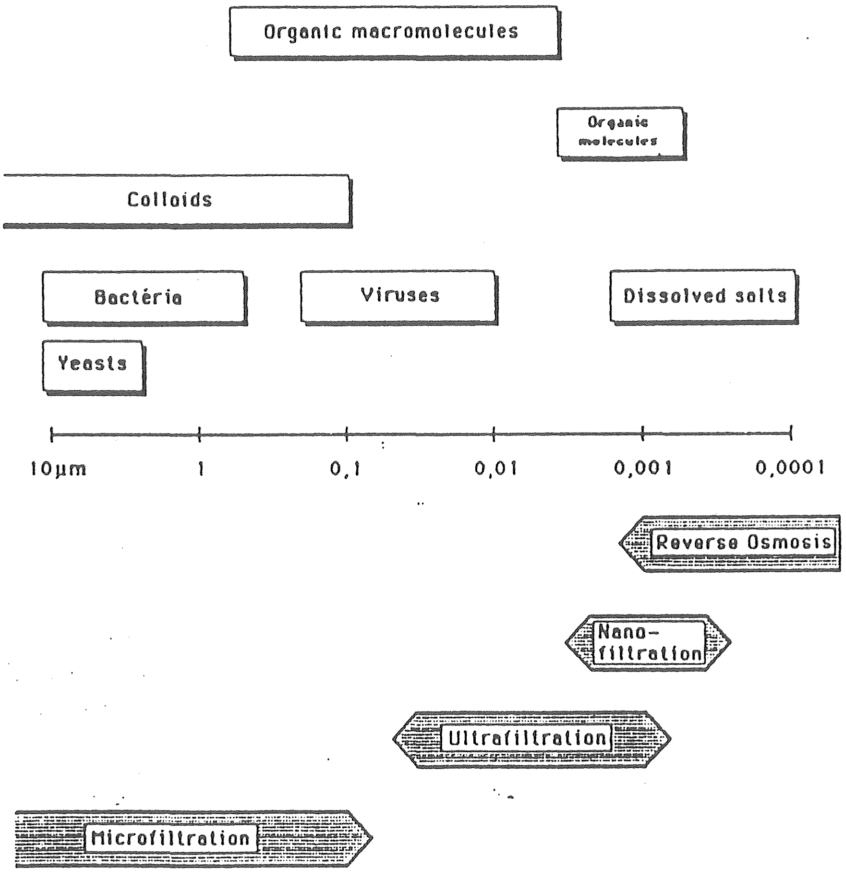

Figure 2.3. Summary of the membrane cut-offs (lower part) and the size of pollutants (upper part) (Bersillon *et al* 1990).

2.9 Ion exchange

Ion exchange processes can sometimes be used to remove small amounts of iron and manganese from water. The choice of resin, cation or anion, depends on which form iron and manganese occur: reduced ionised forms or complexed to negative humic substances.

2.10 Other processes

2.10.1 Well construction

Kronqvist and Sundlöv (1991) have studied treatment methods for acidic well water using two different types of construction around the well where no pumping equipment or electrical supply is needed.

The first method is suitable for wells supplied by shallow ground water. A trench, close to the well, is filled with fine grained limestone mixed with sand. The main part of the inflowing water passes through the trench before reaching the well.

In the second method, an artificial vertical filter of limestone and sand is arranged in a trench near a well. The filter is fed by water via a pipe from the well. After passing through the filter the water is collected in a another well where the water is distributed to the network.

2.10.2 Oxidation within the ground

Hatva *et al* (1973) have described the VYREDOX-iron removal method. The method is based on the idea of oxidation and precipitation of iron within the ground. Practically this is done by pumping water free from iron and saturated with oxygen, into the ground around the well. Using this method of artificial oxidation, a steady gradient is formed in the ground where iron is precipitated and adsorbed in the soil on the oxidised side, and soluble on the reduced side. When water, containing reduced iron, penetrates this gradient, the iron is oxidised and adsorbed.

The gradient zone can be found by measurements of pH and Eh (redox potential). In the gradient zone abundant iron and manganese bacteria are present.

2.10.3 Biological treatment processes

Different kind of bacteria are involved in biological iron and manganese removal (Diem & Stumm 1984, Emerson *et al* 1982, Hallbeck 1993, Hallberg 1988, Hatva *et al* 1985, Lindblad-Påsse 1986, Mouchet 1992, Nealson & Tebo 1980, Robinson & Summerford 1970, Viswanathan & Boettcher 1991).

When organic material are present in addition to iron the removal of both often becomes difficult using chemical methods, without the addition of strong oxidants. Biological removal of iron may solve this problem.

Iron oxidising bacteria like *Gallionella ferruginea* biodegrade iron organic complex and oxidises Fe^{2+}. The oxidation state of iron and manganese is associated with the physicochemical conditions, which can be expressed as Eh and pH. The optimum range of pH and Eh is not the same for iron as for manganese removal. Bacteria precipitating manganese require higher Eh and pH than iron bacteria. Owing to the differences in the optimum treatment conditions for iron and manganese removal, two filtration steps are usually required.

3. METHODS AND MATERIAL

The experimental part of the investigation was performed at the research facility of the Department of Sanitary Engineering, situated at the Lackarebäck water treatment plant, Göteborg.

The properties of filter materials were examined in ten pilot columns. Each column was constructed of Plexiglas. The inner diameter was 6 cm and the length 2.0 m. The columns could be used either for down flow or up flow. Figure 3.1 illustrates four of the columns and the water feed system. One column was equipped with through-the-wall sampling tubes.

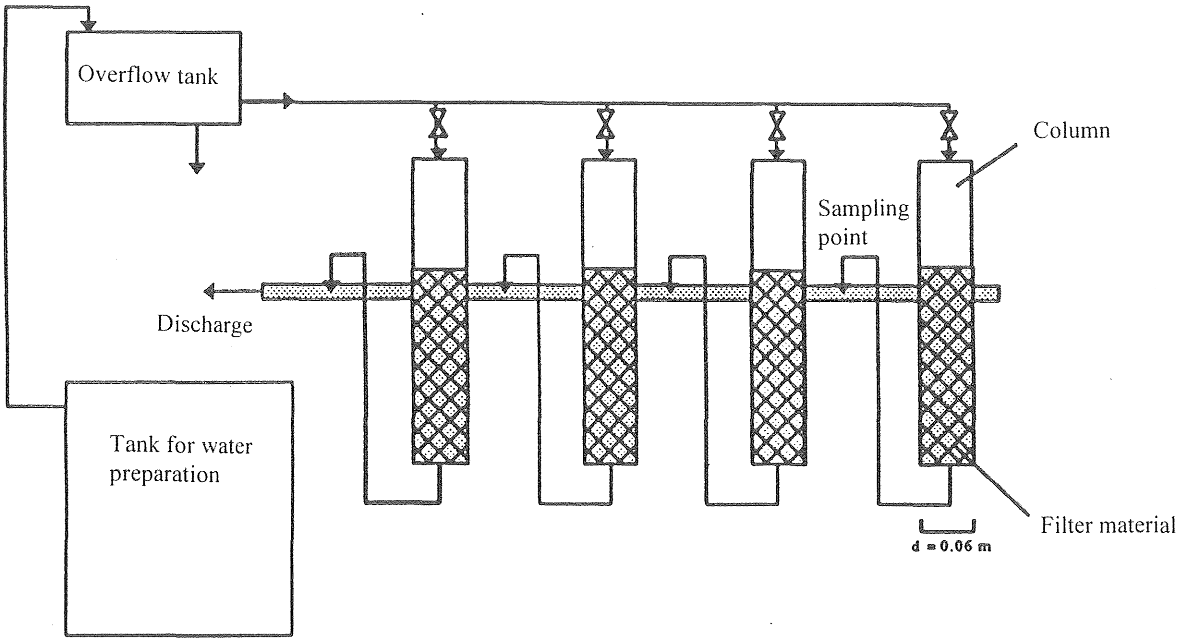

Figure 3.1 Pilot columns.

The raw water to be treated was pumped either to an overflow tank and then, via flow controlled valves or direct via the flow controlled valves, to the top or the bottom of the columns. The pilot filter columns could be used either for down flow as in figure 3.1 or for up flow. The bottom of each column was equipped with a nozzle to retain the filter material.

3.1 Raw water composition

3.1.1 Neutralisation process

The neutralisation process and its effect on the treated water depends on the raw water composition. Therefore two types of water were examined - a very soft water with low hydrogen carbonate concentration and a medium hard water with higher buffer capacity, (see table 3.1). The iron and manganese concentrations were consistently low (Fe<0.05 mg/l, Mn<0.03 mg/l).

Table 3.1 Types of water and chemical composition.

Type of water	pH	HCO_3^- [mg/l]	Total hardness [mg Ca/l]	Free CO_2 [mg/l]
Water 1	5.8-7.0	6-11	10-14	4.2-4.9
Water 2	6.2-6.8	32-41	29-35	33-39

Rapidly filtered water, after chemical precipitation at the water treatment plant was fed in a tube to the research facility for production of Water 1 and 2. The composition of Water 1 (the soft water), corresponded to the rapidly filtered water while Water 2 (the hard water) had to be prepared by adding $Ca(OH)_2$, $CaCl_2$ and CO_2 to it in a 2000 l tank.

3.1.2 Iron and manganese removal

When iron and manganese removal was studied, water with various hardness, iron and manganese concentrations were used, (see table 3.2 and 3.3). The varieties of water were mixed in a 2000 l tank using the rapidly filtered water. After pH adjustment to pH<6 with HCl, varying amounts of iron and manganese were added. Adjustment to pH<6 was performed to prevent precipitation of iron prior to the filter columns. The total hardness of the water was adjusted in the same way as for the neutralisation tests.

Some tests were performed with water containing organic matter. For those tests, surface water from lake Delsjön, the raw water source for the Lackarebäck water treatment plant, was used. To this very soft surface water, iron and manganese were added. The total hardness of the water was increased in some cases.

Table 3.2 Types of raw water treated with calcareous filter material.

Water type	pH	HCO_3^- [mg/l]	Total hardness [mg Ca/l]	Fe [mg/l]	Mn [mg/l]	TOC [mg/l]
Soft water	<6	6-11	15-19	0-2	0-0.5	2
Hard water	<6	34-40	30-36	0-2	0-0.5	2
Soft water with organic matter	<6	<0.5	12	2	0.5	4
Hard water with organic matter	<6	35-40	30	2	0.5	4-4.5

Table 3.3 Types of raw water treated with catalytic filter material.

Water type	pH	HCO_3^- [mg/l]	Total hardness [mg Ca/l]	Fe [mg/l]	Mn [mg/l]	TOC [mg/l]
Soft water	6-7	12-20	13-20	<0.03-2.5	1-5	2
Hard water	6.2	45	42	<0.03	1.5	2
Soft water with organic matter	6-7	16	13	<0.03-1.8	0.7-1.7	4.5

3.2 Calcareous filter materials

The most common calcareous filter materials available on the market were tested, (table 3.4). Four limestone filter materials and three semicalcined dolomite filter materials were used. The particle size was determined by Horkeby (1992) and the specific weight was determined by Horkeby and Björklund (1995).

Table 3.4 Calcareous filter materials.

Filter material	Type	Grain size [mm]	Specific weight [g/cm^3]
Hydrokarbonat	limestone	0.7-1.4	2.8
Filtercarb	limestone	1.2-1.8	
Filtercarb	limestone	0.8-1.2	
Hydrolit Ca	limestone	2.0-6.0	
Hydrolit Ca	limestone	1.0-5.0	2.4
Aqua Ring	limestone	4.0-11	
Magno Dol KI	semicalc. dolomite	0.5-2.5	2.8
Magno Dol KII	semicalc. dolomite	2.0-4.5	
Akdolit Gran 0	semicalc. dolomite	0.5-1.2	2.6
Akdolit Gran 1	semicalc. dolomite	0.5-2.5	
Akdolit Gran 2	semicalc. dolomite	2.0-4.5	
Redolit	semicalc. dolomite	1.0-3.0	2.8

3.3 Catalytic filter materials

Three different catalytic filter materials, (see part 2.4), were examined for their capacity for reducing iron and manganese at different operational conditions and water qualities. Table 3.5 shows the grain size (based on product information) and specific weight (Horkeby and Björklund 1995) for each catalytic filter material.

Table 3.5 Catalytic filter materials.

Catalytic filter material	Grain size [mm]	Specific weight [g/cm^3]
Manganese Greensand	0.3-0.35	2.8
Birm	0.49 and 0.61	1.5
Manganese Dioxide	0.355-0.850	4.3

4. RESULTS

4.1 Neutralisation process

The overall process of the neutralisation of acidic water by crushed limestone or semicalcined dolomite is controlled by different parameters, such as the properties of the filter materials and raw water composition.

4.1.1 Crushed limestone

As acidic water passes through a packed bed of crushed limestone, calcium carbonate dissolves and the pH, calcium concentration and alkalinity increase, while carbon dioxide decreases. The process approaches reaction equilibrium (see reaction 2-2) at pH values of around 8 to 9 for soft water and around 7.5 to 8 for hard water.

Results from the experiment indicate that limestone is suitable for treating very soft water with relatively low concentrations of carbon dioxide. The treated water will then meet limits for pH (7.5-9.0) recommended by the National Swedish Food Administration.

In figure 4.1, pH is plotted as a function of empty bed contact time (EBCT) in a contact bed containing Filtercarb with a grain size of 1.2-1.8 mm. After about 5 minutes of empty bed contact time, the pH value of the treated soft water was slightly below equilibrium pH.

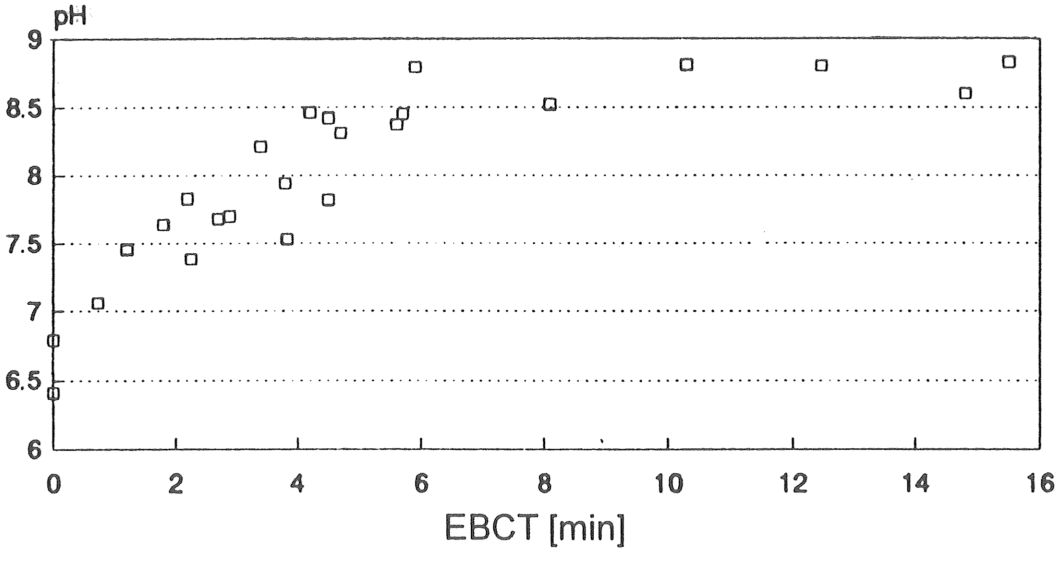

Figure 4.1 Effluent pH as a function of empty bed contact time. Filter material: Filtercarb, 1.2-1.8 mm. Water type: soft.

Results from the investigation using different kinds of limestone material, shows that pH values of treated water vary with composition of filter material, grain size and flow conditions.

When water was treated with Hydrolit Ca, equilibrium pH was achieved after an empty bed contact time of only 2-3 minutes. This is dependent on magnesium hydroxide formed from the high content of magnesium oxide in Hydrolit Ca compared to other limestone filter materials.

Water treated with the pure limestone Aqua Ring, with a grain size of 4-11 mm, needed an empty bed contact time of more than 40 minutes to achieve equilibrium pH.

The total hardness of the water increases after filtration through pure limestone, due to the reaction between $CaCO_3$ and CO_2. After 10 minutes empty bed contact time, the total hardness increased by 50%. The concentration of magnesium did not change during the filtration through pure limestone, but increased slightly after filtration through Hydrolit Ca.

The change in alkalinity is dependent on the concentration of carbon dioxide in the raw water according to the reaction:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad (4\text{-}1)$$

Both calcium and hydrogen carbonate concentrations have a significant effect on the reaction rate between CO_2 and $CaCO_3$. Increasing concentrations will increase the empty bed contact time needed to obtain equilibrium. In figure 4.2, pH is plotted as a function of empty bed contact time in a filter bed containing Filtercarb with a grain size of 1.2-1.8 mm, when medium hard water was treated. An empty bed contact time of at least 15 minutes is required to reach the pH (7.5-9) recommended by the National Swedish Food Administration. The concentration of hydrogen carbonate in the water after 15 minutes empty bed contact time was 105 mg/l which corresponds to a free carbon dioxide of 6 mg/l. To mitigate copper corrosion the concentration of free carbon dioxide concentration of less than 0.2 mg/l is to be prefered (Sander *et al* 1996)

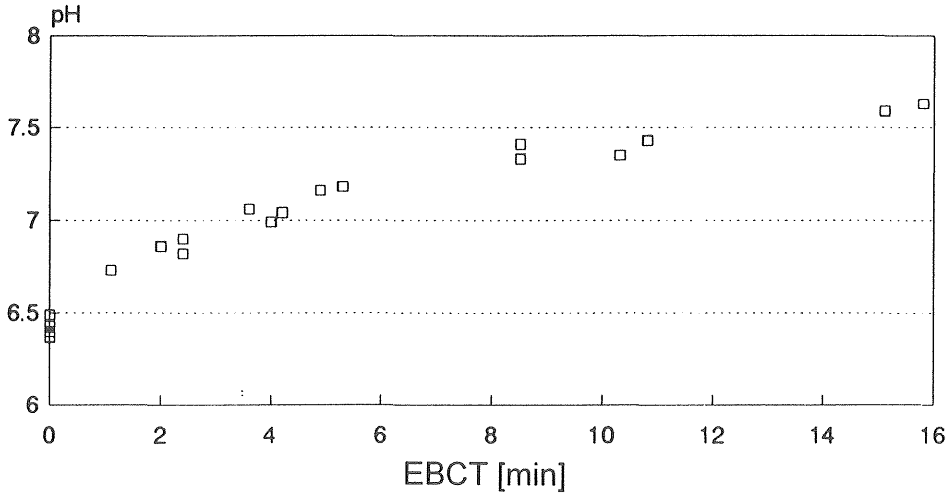

Figure 4.2 Effluent pH as a function of empty bed contact time. Filter material: Filtercarb, 1.2-1.8 mm. Water type: hard.

4.1.2 Semicalcined dolomite

The effluent pH is increased very rapidly when soft water is filtered through semicalcined dolomite. This leads to a high effluent pH which is above the stated limits for drinking water (7.5-9.0). The experiment indicated that it is suitable to filter hard water through semicalcined dolomite. Due to the fact that semicalcined dolomite contains magnesium oxide, hard water will reach a pH-value between 7.5 and 9.0 in a short empty bed contact time. Figure 4.3 shows effluent pH plotted as a function of empty bed contact time when hard water was filtered through Magno Dol with a grain size of 0.5-2.5 mm.

At an empty bed contact time of five minutes the pH of filtered water was 9, hydrogen carbonate concentration 80 mg/l and free carbon dioxide concentration about 0.1 mg/l. To mitigate especially copper corrosion hard water should therefore be filtered through semicalcined dolomite which results in a low free carbon dioxide concentration.

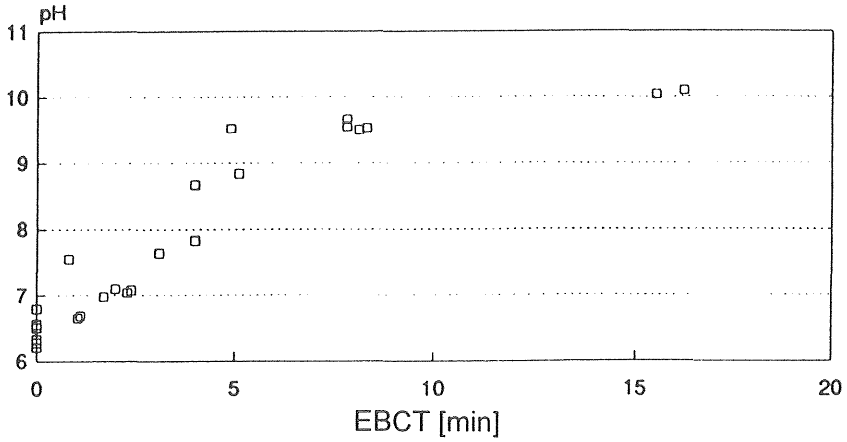

Figure 4.3 Effluent pH as a function of empty bed contact time. Filter material: Magno Dol, 0.5-2.5 mm. Water type: hard.

After 4 weeks of continuous operation of the filter bed, a lower effluent pH is obtained, as a result of a decrease of the magnesium content in the filter material during the filtration. When treating hard water precipitation of calcium carbonate, blocking the particle surface will also lead to a lower effluent pH. Figure 4.4 and 4.5 show effluent pH plotted as a function of empty bed contact time for filtration of soft water through new and four weeks old, Redolit filter material.

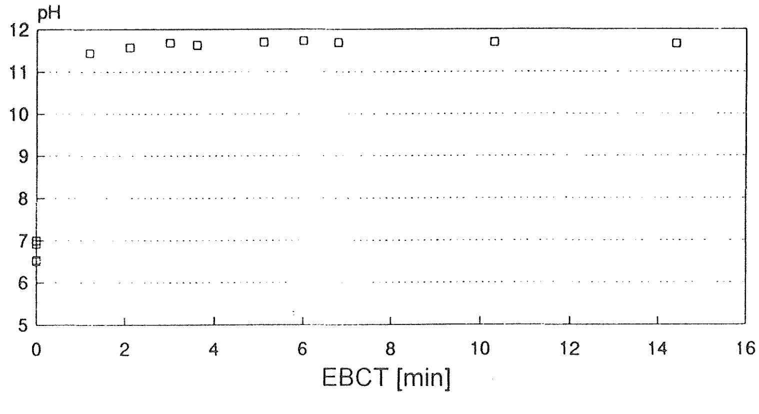

Figure 4.4 Effluent pH as a function of empty bed contact time. Filter material: new Redolit. Water type: soft.

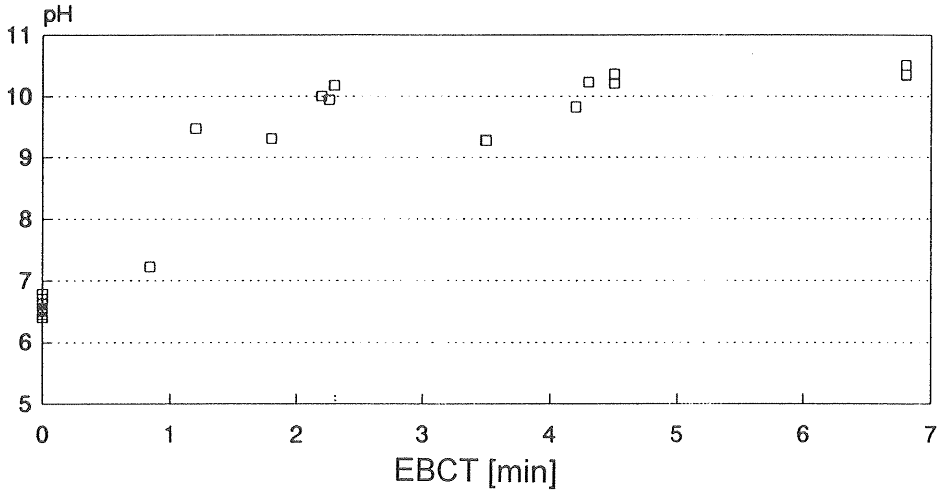

Figure 4.5 Effluent pH as a function of empty bed contact time. Filter material: four weeks old Redolit. Water type: soft.

The increase of total hardness in water after filtration through semicalcined dolomite is dependent on the increase of magnesium ion concentration. The calcium ion concentration is reduced due to the high pH caused by dissolution of magnesium oxide, which leads to precipitation of calcium carbonate. Figure 4.6 shows the total hardness, magnesium and calcium concentration in hard water, after filtration through Akdolit Gran with a grain size of 2.0-4.5 mm.

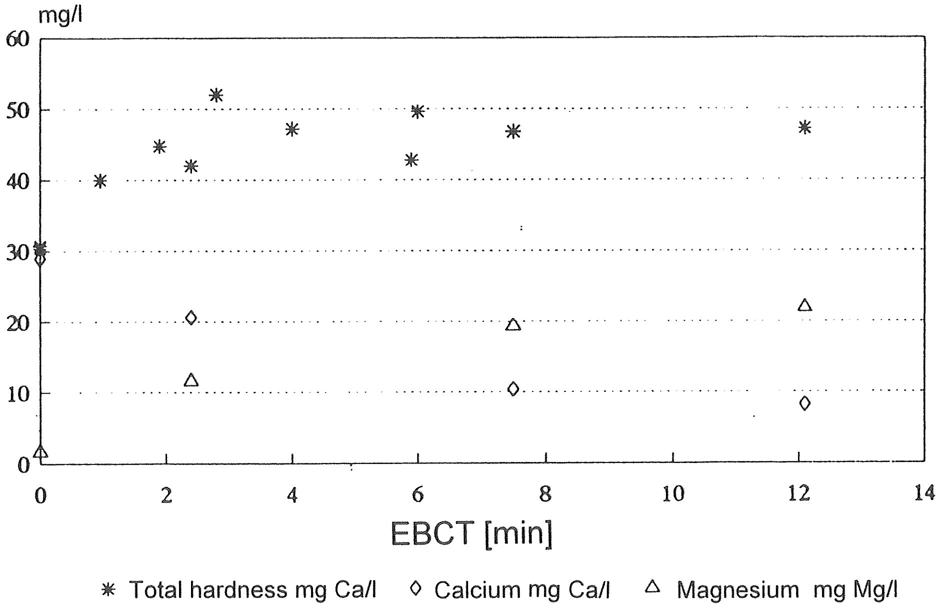

Figure 4.6 Total hardness, magnesium and calcium concentration plotted as a function of empty bed contact time. Filter material: Akdolit Gran, 2.0-4.5 mm. Water type: hard.

The influent concentration of carbon dioxide has a significant effect on the effluent alkalinity. But the ratio between the increase in hydrogen carbonate and the consumed carbon dioxide is lower than corresponding ratio for limestone filtration. That is appearent from the reactions below compared to the reaction for calcium carbonate dissolution, (4-1).

$$MgO + H_2O + 2CO_2 \rightarrow Mg^{2+} + 2HCO_3^-\text{; dissolution of magnesium oxide} \qquad (4\text{-}2)$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O\text{; precipitation of calcium carbonate} \qquad (4\text{-}3)$$

4.1.3 Conclusions

The results from the investigation of calcareous filter materials show that soft, acidic water with a relatively low concentration of carbon dioxide, should be treated with limestone. The equilibrium pH-value will be reached in an empty bed contact time, of about 5 minutes, as the rate of the dissolution reaction (4-1) will be relatively high.

When hard water is treated with limestone the dissolution reaction rate is decreased by the high concentrations of calcium and hydrogen carbonate. This leads to an unacceptably long empty bed contact time to reach a pH over 7.5. For the treatment of hard, acidic water, semicalcined dolomite is recommended instead, as pH will increase in a short time due to the dissolution of magnesium oxide.

In figure 4.7 recommendations for suitable filter material for the treatment of acidic water are given according to concentration of carbon dioxide, total hardness and alkalinity. For the treatment of hard water with a high concentration of carbon dioxide, the aeration process is recommended.

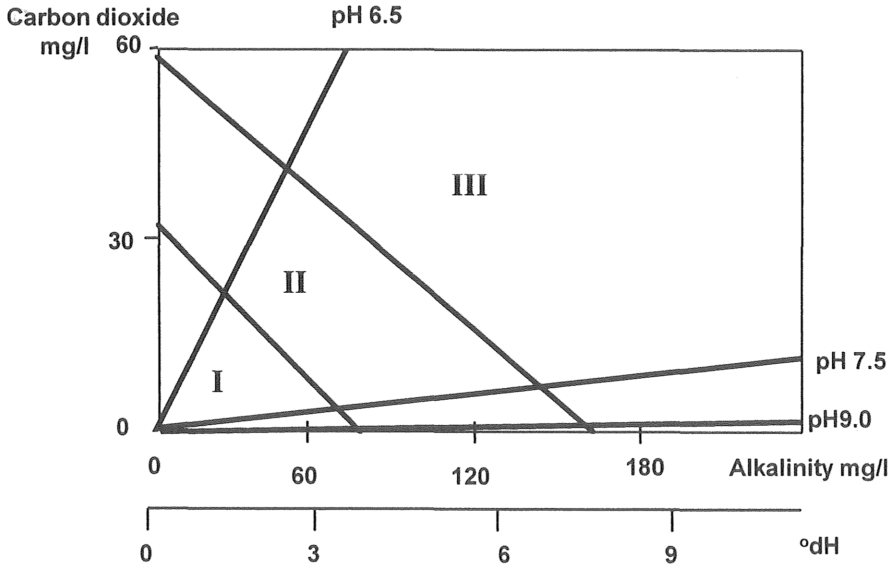

Figure 4.7 Recommended treatment process for acidic water.
I: Filtration through limestone filter material
II: Filtration through semicalcined dolomite
III: Aeration

From the copper corrosion point of view, semicalcined dolomite is a convenient filter material as the carbon dioxide concentration decreases after reaction with magnesium oxide and the calcium concentration decrease due to the precipitation of calcium carbonate.

However, a negative effect of calcium carbonate precipitation is the risk of clogging when the flow through the bed is stopped or very low, which leads to a decrease in the neutralisation capacity.

4.2 Iron and manganese removal

Filter materials, investigated for the removal of iron and manganese were calcareous filter materials (crushed limestone and semicalcined dolomite) and catalytic filter materials (Manganese Greensand, Birm and Manganese Dioxide). Different combinations of calcareous and catalytic filter materials were also investigated.

4.2.1 Iron and manganese removal by calcareous filter materials

The main application for calcareous filter materials is to reduce the corrosive properties of acidic water. Private water supply wells, with acidic ground water, often have problems with high concentrations of iron and manganese, exceeding the drinking water standards. Therefore the neutralisation effect, on water containing iron and manganese, was investigated using different calcareous filter materials. Their ability to remove iron and manganese from ground water was also investigated.

The differences in the removal of iron and manganese by limestone and semicalcined dolomite are mainly dependent on the chemical properties of iron and manganese and the chemical composition of the filter materials as described by Horkeby (1993).

Removal of iron was performed using limestone as well as semicalcined filter material, as the pH-value was high enough in both materials for iron oxidation. Iron is mainly removed by filtration of precipitated iron hydroxide. Figure 4.8 shows iron concentration in the water as a function of bed depth after continuous filtration of 1.5, 27 and 46 hours respectively. The influent water was soft with an iron and manganese concentration of 2.0 and 0.5 mg/l respectively and the filter material in the up flow filter was Hydrokarbonat. The flow was 7.5 m/h (350 ml/min). The results show that iron was removed in the first 20 cm of the filter bed. After 48 hours of continuous filtration the first 3 cm of the bed was saturated with iron. A conventional filter is however back-washed after an operating time corresponding to 1-2 hours continuous filtration.

In filtration tests with down flow filtration, the iron removal was even more effective in the first part (top layer) of the filter bed than in the up flow filter in which the first part (bottom layer) consisted of coarser grain size, due to the back-washing procedure. Down flow filtration is also prefered to avoid precipitated iron hydroxide in the treated water at high flow rates in the filter bed during high water consumption.

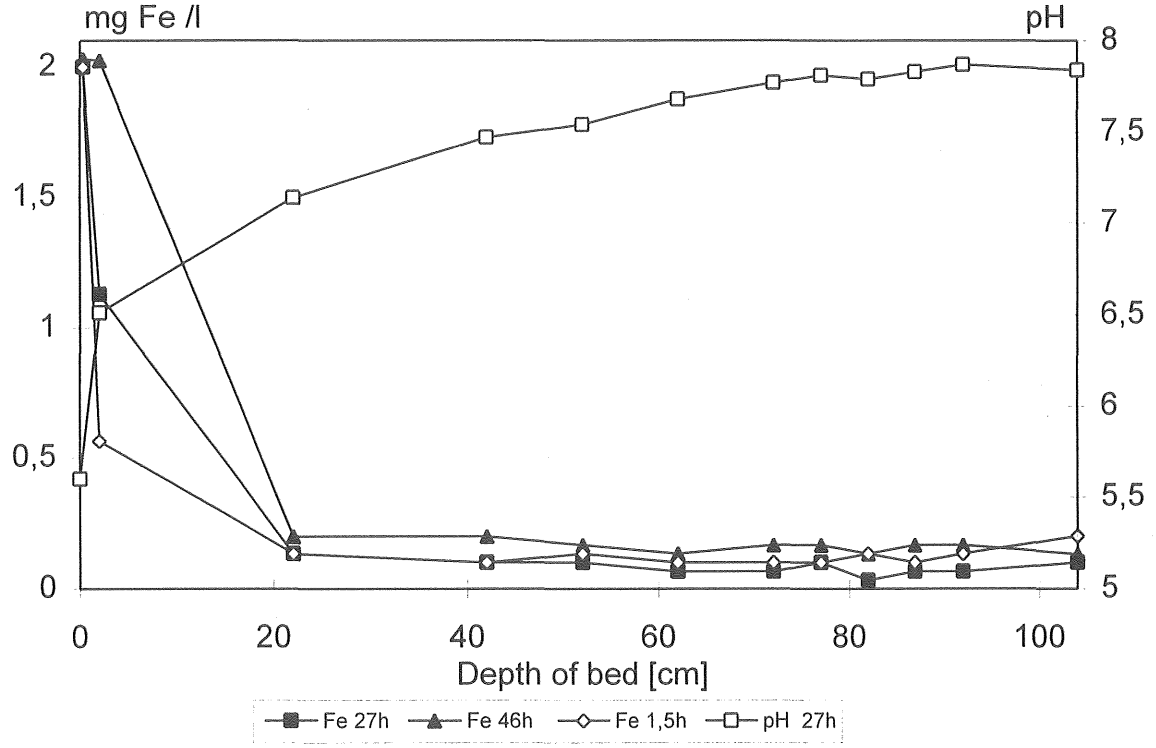

Figure 4.8 Iron concentration and pH in filtered water as a function of bed depth at different operation times. Filter material: Hydrokarbonat. Water type: soft.

An acceptable manganese removal was obtained only in the semicalcined dolomite filter bed and at a pH-value over 9 in treated water. The manganese removal increases with increasing pH. Figure 4.9 shows manganese concentration and pH in the treated water, as a function of bed depth. The filter material used was Redolit and the filter was in an up flow operation mode. The flow was aproximately 9 m/h.

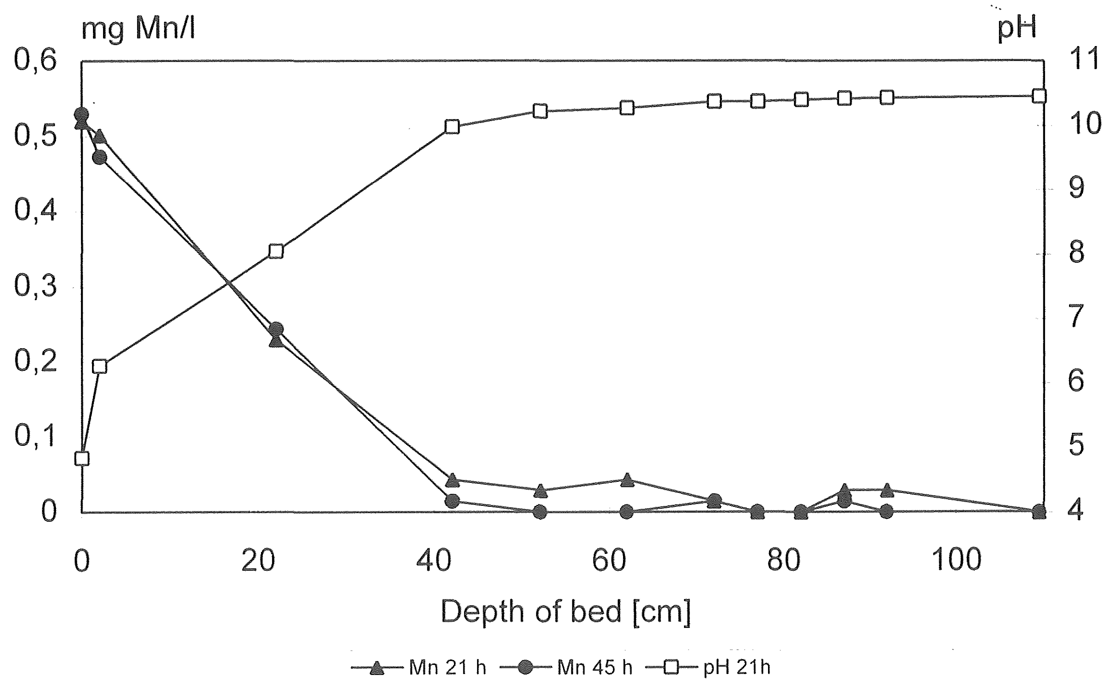

Figure 4.9 Manganese concentration and pH in filtered water as a function of bed depth at different operation times. Filter material: Redolit. Water type: soft.

Filtration tests with varying fluid velocity show that the manganese removal increases when the diffusion layer decreases with increasing velocity.

Results from the filtration tests show that the neutralisation effect of the filter material is affected by the iron and manganese concentration in the water. Precipitation and adsorption of iron and manganese on the surface of the particles decreases the active surface area of the filter material. Manganese, as opposed to iron, precipitated closer to the surface area due to the pH-gradient from the material surface to the bulk solution, see figure 4.10. Most of the iron is precipitated in the bulk solution, while manganese is precipitated closer to the particle surface and some of the manganese ions adsorbs or precipitates in the pores of the filter material. This leads to the conclusion that manganese has a more negative influence than iron on the neutralisation effect.

The neutralisation efficiency is influenced by the total pore surface of the filter material. Iron and manganese can penetrate into the pores and remain after back-washing.

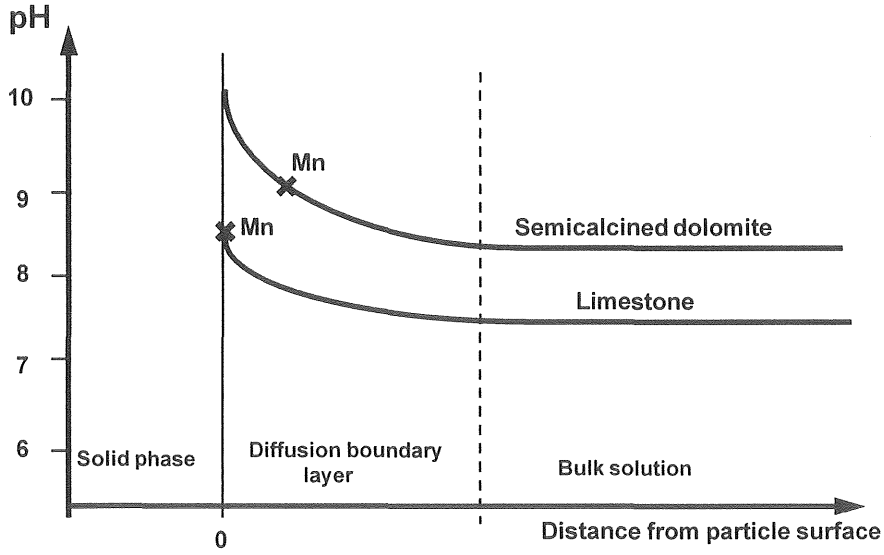

Figure 4.10 Schematic diagram illustrating the pH-gradient from the material surface to the bulk solution. The points at which manganese is precipitated or adsorbed are indicated.

As previously discussed, the removal of iron and manganese is dependent on the chemical composition of the filter material. But the result is also influenced by the structure of the filter material.

To explain the removal mechanism of iron and manganese in calcareous materials, porosity was analysed before and after filtration of water containing iron and manganese. The pore surface area and pore volume were determined by the measurement of the nitrogen adsorption isotherm, which is described in detail by Horkeby & Björklund (1995). Results from the porosity analyses are summarised in table 4.1 and 4.2.

Table 4.1 Pore surface area, pore volume and average pore diameter for filter materials before filtration.

Filter material	Macropore surface area [m^2/g]	Micropore surface area [m^2/g]	Macropore volume [cm^3/g]	Average pore diameter [nm]
Hydrokarbonat	0.38	0.01	0.0014	13
Hydrolit Ca	3.89	0.15	0.0120	11
Redolit	4.43	0.26	0.0185	20
Magno Dol KI	6.71	0.69	0.0295	21
Akdolit Gran 1	5.97	0.71	0.0387	25

The total surface area of Hydrokarbonat is very small compared to the other filter materials. This is one reason why the neutralisation efficiency of Hydrokarbonat is unaffected by iron and manganese in the water, because there are very few pores that can be penetrated by iron and manganese.

Table 4.2 Pore surface area, pore volume and average pore diameter for filter materials after filtration.

Filter material	Macropore surface area [m^2/g]	Micropore surface area [m^2/g]	Macropore volume [cm^3/g]	Average pore diameter [nm]
Hydrokarbonat	0.32	<0.01	0.0011	14
Hydrolit Ca	5.09	0.28	0.0125	9.8
Redolit (1)	7.05	<0.01	0.0245	14
Redolit (2)	6.19	0.14	0.0301	19
Magno Dol KI	9.17	0.52	0.0435	19
Akdolit Gran 1	12.07	1.01	0.0497	16

Micropores were defined as pores with a diameter of < 1.7 nm and macropores with a diameter of 1.7 - 300 nm.

In table 4.3 total amount of metal in water filtered, before porosity analysis, is summarised for each filter material.

Table 4.3 Total amount of iron and manganese filtered per litre of filter material (influent concentration multiplied by total filtered volume) and the corresponding time of filtration.

Filter material	Iron [mg/l filter material]	Manganese [mg/l filter material]	Time of filtration [h]
Hydrokarbonat	731	149	70
Hydrolit Ca	806	168	80
Redolit (1)	1122	287	110
Redolit (2)	586	119	60
Magno Dol KI	601	236	60
Akdolit Gran 1	458	237	50

As calcareous filter materials are dissolved by acid water, the shape of the grains changes during the filtration process. All examined filter materials, except Hydrokarbonat, increased in pore surface area and decreased in pore diameter after the treatment of acidic water containing iron and manganese. Hydrokarbonat however, decreased in pore surface area but had almost no change in pore diameter, see figure 4.11. These results show that semicalcined dolomite is more soluble than limestone, which leads to increased pore surface area when the magnesium oxide is released from the material. Two different porosity analyses of Redolit show that increased amount of treated water with iron and manganese, results in increased pore surface area and decreased pore diameter. The decrease in pore diameter is probably an effect of iron and manganese adsorbed in the pores.

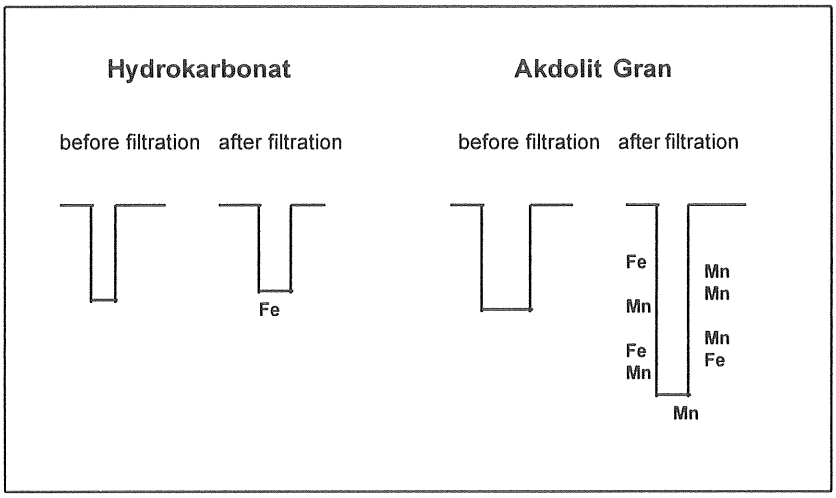

Figure 4.11 Schematic description of pores before and after filtration.

The shape of the pores also influences the removal mechanism of iron and manganese and the neutralisation efficiency. The total pore surface area of Magno Dol is the largest one, while the largest pore volume is found for Akdolit Gran which has cylindrical pores open at both ends, compared to Magno Dol which is a mixture of tapered and wedge-shaped pores with open ends. It is easier for metals to penetrate into the pores of Akdolit Gran than Magno Dol, owing to the different shape. The pores of Redolit are of the same type as those of Magno Dol.

4.2.1.1 Conclusions

The investigation of the properties of calcareous materials in contact with acidic water containing iron and manganese shows that:

- Limestone filter material could be used for the removal of iron if the filter is back-washed regularly.
- Semicalcined filter materials could be used for the removal of iron and manganese but the neutralisation efficiency will be negatively affected.

4.2.2 Catalytic filter material

When treating acid water containing iron and manganese it is common to mix catalytic filter material with calcareous filter material in the same unit.

4.2.2.1 Manganese Greensand

The different combinations of Manganese Greensand and calcareous filter material examined, are described schematically in figure 4.12.

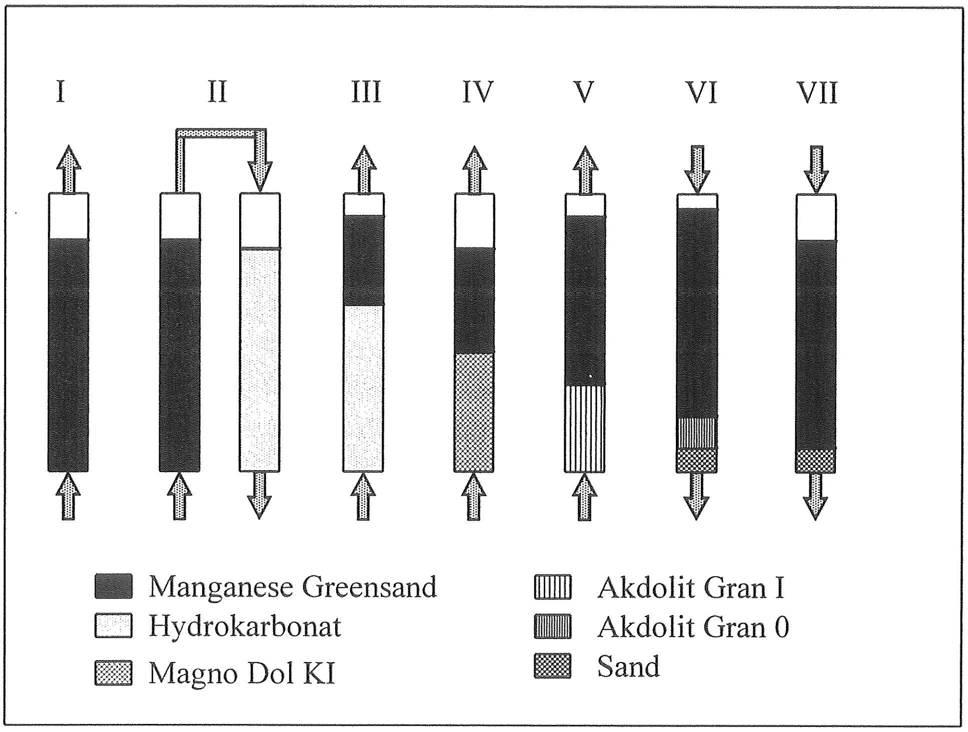

Figure 4.12 Combinations of Manganese Greensand and calcareous filter material examined.

Filtration tests with different concentrations of manganese (2, 3 and 5 mg/l) in the influent water where performed. The iron concentration was also varied to show the effect on iron removal but also the influence on manganese removal. The catalytic filter material Manganese Greensand was effective for the removal of manganese, even if the influent concentration was as high as 5 mg/l and the concentration of iron was less than 0.05 mg/l. The maximum concentration of manganese in effluent water was 0.06 mg/l. The removal effect was however decreased if the influent concentration of iron was 1 mg/l or more. With reference to the test below, figure 4.13, where the influent manganese concentration was 2.4 mg/l and the influent iron concentration was 1.0 mg/l, the decreased effect was a result of the filter material being blocked by iron.

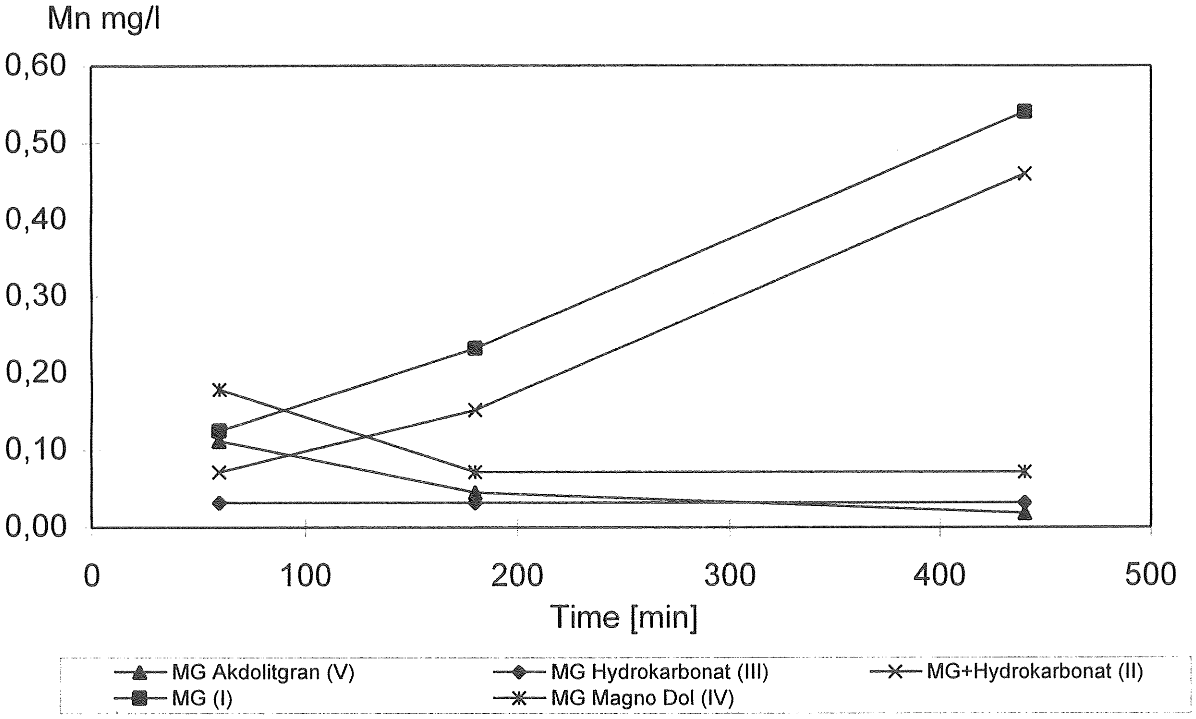

Figure 4.13 Effluent manganese concentration as a function of time of filtration. The Roman numerals corresponds to filter combinations in figure 4.12.

The manganese removal in water with an iron content of ≥1 mg/l was more effective if Manganese Greensand was mixed with calcareous filter material. As up flow filters were used, iron was removed in the calcareous material at the bottom before passing it through Manganese Greensand.

The most effective iron removal was obtained in the down flow Hydrokarbonat filter that was connected after the Manganese Greensand filter. The manganese removal was however, not as effective with this combination. But if the Hydrokarbonat filter is placed prior to the Manganese Greensand filter, as in column III, the removal of both iron and manganese is effective. This column was however operated using up flow. As most iron is precipitated in the bulk solution, down flow filters are preferable due to the better filtration effect.

Studies were also undertaken to investigate the affect of organic matter on the removal of iron and manganese. No significant negative effect could be observed when the maximum concentration of organic matter was 5 mg TOC/l, which is a relatively high concentration.

In one filtration test, the back-washing of the two down flow filters (VI, VII) was performed using raw water with a manganese content of 0.8 mg/l. Result from this test indicates that manganese concentration in the filtered water is increased after back-washing. This is probably caused by manganese accumulation in the bottom layer during back-washing, which affects the water quality when the filter brought into operation. Therefore it is recommended to use treated water, free from iron and manganese for the back-washing.

4.2.2.2 Birm

Table 4.4 shows the different combinations of filter material tested in the filter columns.

Table 4.4 Combinations of Birm and calcareous filter materials examined.

Combination	Catalytic filter material	Bed depth [cm]	Calcareous filter material	Bed depth [cm]
I	Birm regular	40	Akdolit Gran 1	30
II	Birm regular	40	Akdolit Gran 1 Akdolit Gran 0	10 10
III	Birm regular	100		
IV	Birm fine	90		

The catalytic filter material, Birm, was also effective for the removal of manganese in water free from iron. At an influent concentration of 5 mg Mn/l, the maximum effluent concentration was <0.06 mg Mn/l. In the presence of both iron and manganese (1 resp. 2 mg/l) in the influent water, the removal of manganese was decreased in comparision to water free from iron.

A reduced efficiency for both iron and manganese removal was significant after continuous filtration of more than 200 minutes (see figure 4.14 and 4.15). As a consequence of this, back-washing is recommended after 1-2 hours of continuous filtration. For a normal operation in a household this corresponds to a daily backwash.

Filtration tests using soft water containing organic matter of 3 mg TOC/l showed a negative effect on the manganese removal in water free from iron.

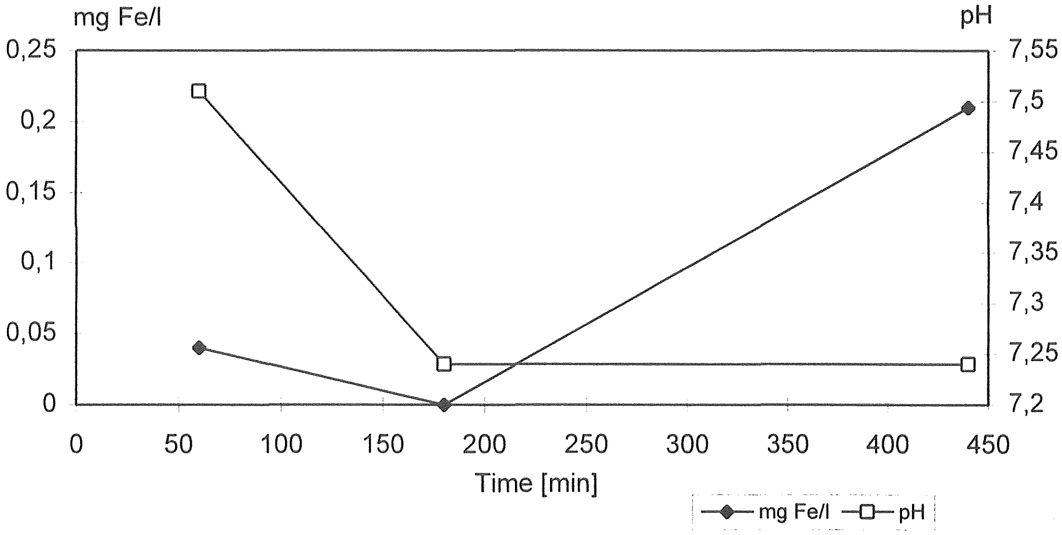

Figure 4.14 Effluent iron concentration and pH as function of filtration time.

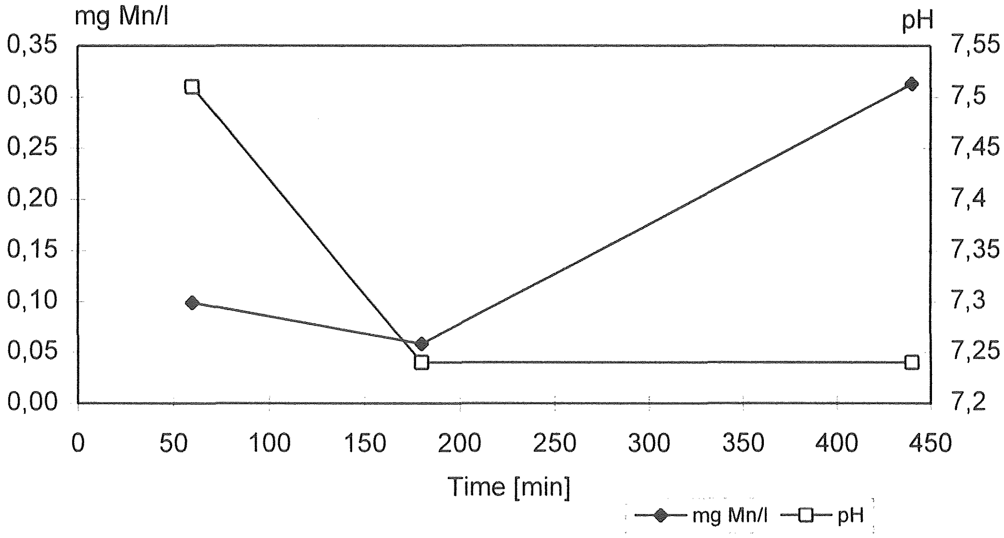

Figure 4.15 Effluent manganese concentration and pH as function of filtration time.

4.2.2.3 Manganese Dioxide

Only a few tests were performed with Manganese Dioxide and two different combinations of filter contact beds were examined, see table 4.5.

These early results indicate that the removal of iron and manganese with Manganese Dioxide, seems to be poorer than with other catalytic filter materials. However after a period of operation the removal of iron and manganese seems to increase, probably due to manganese dioxide formation on the sand grains. The empty bed contact time ought to be at least 10 minutes. Manganese removal in hard water was more effective in the filter combination with Akdolit Gran, Manganese Dioxide and sand, than the filter combination with only Manganese Dioxide and sand.

Table 4.5 Combinations of Manganese Dioxide and calcareous filter materials examined.

Combination	Catalytic filter material	Bed depth [cm]	Calcareous filter material	Bed depth [cm]
I	Manganese Dioxide	16	sand	64
II	Manganese Dioxide	16	sand Akdolit Gran	44 20

4.2.2.4 Conclusions

- Filtration through Manganese Greensand is a very effective method for the removal of manganese in water free from iron. When treating water with an iron concentration of > 1 mg Fe/l, aeration or filtration through Hydrokarbonat prior to the Manganese Greensand filter is recommended. When treating acidic water with a high concentration of manganese it is recommended to filter the water through Hydrokarbonat after the Manganese Greensand filter, in order to increase pH.

- Filtration through Birm is also an effective method for the removal of managnese from water. But like Manganese Greensand, iron has a negative effect on the treatment result. The presence of organic carbon (> 3mg TOC/l) will also have a negative effect on the result.

- Removal of iron and manganese with Manganese Dioxide filter material is probably more effective after a period of operation long enough to deposit a manganese dioxide layer on the sand grains. The experiments carried out here were to short and need to be repeated.

4.3 Expansion during back-washing

Back-washing properties for the filter materials were studied. Back-washing was performed with water. The bed expansion was recorded at different back-wash flows. In figure 4.16, bed expansion by % of bed depth are plotted as a function of flow, in m/h.

In filter units for private households it is common to mix catalytic filter materials with calcareous filter materials. This can however lead to reduced effect of the calcareous material due to ineffective back-washing. As calcareous filter materials require a higher back-wash rate than catalytic filter material, (see figure 4.16), the calcareous filter materials will not fluidize during back-washing in beds mixed with Manganese Greensand or Birm.

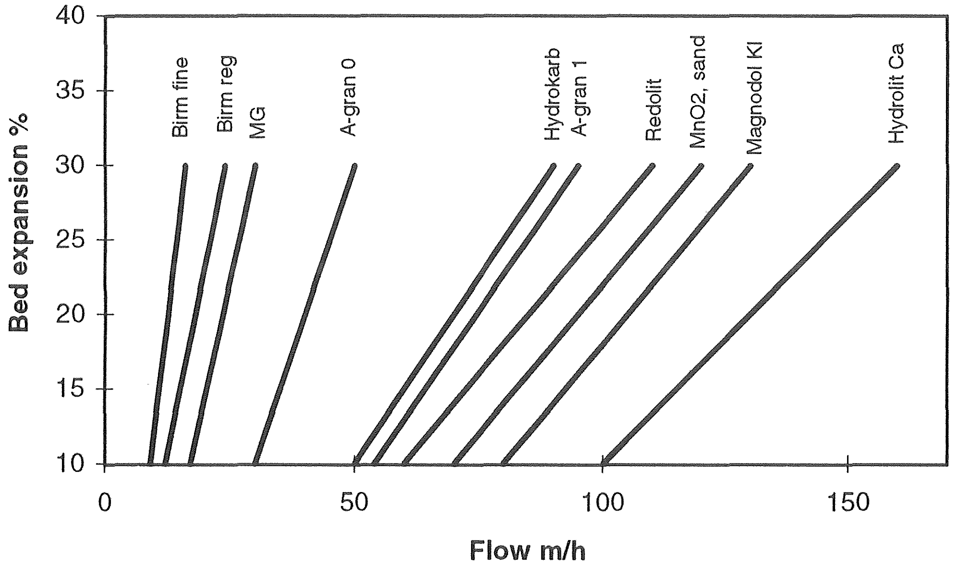

Figure 4.16 Bed expansion as a function of back-wash flow.

5. CONCLUSIONS AND PRACTICAL APPLICATIONS

5.1 The neutralisation process

- When treating acidic water with calcareous filter material it is important to know the composition of the water (pH, total hardness, alkalinity and the concentration of carbon dioxide, iron and manganese) for the correct choice of filter material.

- Limestone with minimum impurities ($CaCO_3$>99%) and a grain size of 1-2 mm, is suitable to use for the treatment of very soft water with a low concentration of carbon dioxide.

- Semicalcined dolomite is suitable for the treatment of medium hard water with a carbon dioxide concentration up to 30 mg/l or soft water with high carbon dioxide concentration (> 30 mg/l).

- For the treatment of hard water with a high concentration of carbon dioxide (> 30 mg/l), aeration is prefered in order to reduce excessive carbon dioxide, before filtration through semicalcined dolomite.

- Semicalcined dolomite filter units should be in continuous operation to avoid high effluent pH and clogging of the filter material. In the case of intermittent operation, the pH of the water will exceed the equilibrium pH. This in turn leads to precipitation of calcium carbonate, clogging of filter material and reduced active surface.

- Iron and manganese in the raw water influences the deacidification efficiency of calcareous filter material. This effect is more significant for manganese than for iron, due to the fact that manganese precipitates closer to the particle surface and a higher amount is adsorbed. Most obvious is this effect for semicalcined dolomite.

- It is important to back-wash the neutralisation filter regularly, at least once a week, to remove suspended solids from the filter bed. If the water is subject to greater contamination, i.e. iron and manganese, back-washing must be carried out more often and in relation to filter head loss.

5.2 Iron and manganese removal

- Iron is precipitated as iron hydroxide in the bulk solution of a neutralisation filter. Iron hydroxide is then removed by filtration in the filter material. Down flow is to prefer to avoid iron hydroxide in the treated water at high flow rates in the filter bed. The removal of iron is high in both limestone and semicalcined filter materials.

- Manganese is removed by the neutralisation filter as precipitated and filtrated manganese dioxide and by adsorption in the pores of the filter grains. The precipitation increase with increasing pH. To get an acceptable manganese concentration in effluent water, pH must be >9. Therefore the removal is very poor in limestone filter material, and high in semicalcined filter material.

- Iron and manganese removal are dependent on the shape (porosity and grain size) of the filter material. Iron removal increases with decreasing grain size and manganese removal increases with a larger total pore surface area.

- The few experiments performed with organic material are in aggrement with results reported in the literature which states that organic matter influences iron and manganese removal because the metals are complexed by dissolved organic carbon. This leads to decreased oxidation and precipitation, which is most significant for iron with a high degree of complexation.

- In the case of deacidification of acidic water in neutralisation filters, up flow is commonly used to obtain movement in the bed. This is not recommended for water containing iron and manganese, because the risk of precipitated iron and manganese in the effluent. Down flow is preferred instead.

- Careful maintenance is important when using catalytic filter material. After each service cycle, corresponding to 2 hours continuous operation, the filter should be back-washed to remove the suspended material collected during the run. Back-washing with filtered water is recommended to avoid precipitation of iron and manganese, in the bottom of the filter, and contamination of the effluent at the beginning of next service cycle. The Manganese Greensand bed should be regenerated, continuously or intermittently, with potassium permangate solution. The catalytic filter materials, Birm and Manganese Dioxide do not require regeneration, but oxygen concentration in the water is necessary for the oxidation reaction.

- Manganese removal by catalytic filter material is more effective in the absence of iron in the water. High iron content could be removed by aeration or by a limestone filter bed prior to the catalytic filter bed. In the case of the treatment of acidic water containing manganese, a limestone bed could be placed after the catalytic bed instead, in order to increase pH of the treated water.

- When Manganese Greensand or Birm are mixed with calcareous filter material, consideration should be given to the different back-washing properties of each filter material. In order to achive acceptable back-washing for both filter materials, a calcareous filter material with a small particle size is recommended e.g. Akdolit Gran 0. Another, but more expensive alternative, is to place the filter material in separate filter units.

6. SUGGESTIONS FOR FURTHER WORK

- In the work undertaken, only short-term studies were performed due to the time constraints of the project. Long-term studies should provide valuable information about the filter materials and operation experience of the filter units for acidic water containing iron and manganese.

- Similar investigations should be performed with natural ground water with different compositions. In the present study influent water was saturated with oxygen, which is not typical of ground water. Oxygen concentration and redox potential, influence the precipitation properties of iron and manganese. The presence of other components in ground water can also affect the treatment result.

- The possibility of using a fraction with smaller grain size of calcareous material should be investigated to match the back-washing properties with the catalytic filter material.

- Development and testing of a system with separate filter units for calcareous and catalytic filter material should be investigated in order to make it possible to perform more effective back-washing and avoid negative effects like the reduced neutralisation effects of calcareous materials caused by manganese.

- Treatment of acidic water containing iron, manganese and of organic matter is a common problem in small systems. As the amount of organic matter in ground water has increased over recent years, the demand for a suitable treatment system is expected to grow. The treatment of water with organic matter should therefore be studied in order to obtain more information about the processes suitable for small systems.

7. REFERENCES

Baier, J.H., Lykins, B.W., Fronk, C.A., Kramer, S.J. (1987) Using Reverse Osmosis to Remove Agricultural Chemicals from Groundwater. J. AWWA 79:8:55-60.

Baldauf, G. (1986) Verfahren zur Aufbereitung von Sauren, Schwermetall - und/oder aluminiumhaltigen Rohwässern, Pat. No. 3631218

Baozhen, W., Jinzhi, T., Jun, Y. (1985) Purification of Polluted Source Water with Ozonation and Biological Activated Carbon. Ozone: Science and Engineering 6:245-260.

Beeftink, W.G. (1976) Groundwaterzuivering Pompstation Valtherbos. H_2O 9:24:499-502.

Bersillon, J.L., Anselme, C., Mallevialle, J., Aptel, P. (1989) L'utrafiltration appliquee au traitement de l'eau potable: le cas d'un petit systeme. Eau, Ind., Nuisances, 130:61-64.

Bersillon, J.L., Anselme, C., Mallevialle, J., Fiessinger, F. (1990) Ultrafiltration Applied to Drinking Water Treatment: Case of a Small System. Water Supply, 8(3-4, Water Nagoya 89) 209-219.

Briggs, M. (1993) Iron & Manganese Removal from Potable Waters. LRSC. MICorr, GIEnvSc, Chemical and Abrasive Sales.

Börner, H. (1961) Die Aufbereitung von Grund- und Oberflächenwässern unter besonderer Berucksichtigung dolomitischer Filtermaterialen. Neue DELIWA-Zeitschrift, Hannover 1961,Heft 1.

Clack Corporation (1993) Information material. Clack Corporation, 4462 Duraform Lane P.O. Box 500 Windsor, Wisconsin 53598-0500 USA.

Cleasby, J.L. (1975) Iron and Manganese Removal - A Case Study. J. AWWA 67:2:147-149.

Degrémont, (1973) Water Treatment Handbook,4:th ed.

Diem, D., Stumm, W. (1984) Is Dissolved Mn^{2+} being Oxidized by O_2 in Absence of Mn-bacteria or Surface Catalysts? Geochimica et Cosmochimica Acta 48:1571-1573.

DIN 19621 (okt. 1973) Dolomitisches Filltermaterial zur Wasseraufbereitung.

Emerson, S., Kalhorn, S., Lucinda, J. (1982) Environmental Oxidation Rate of Manganese(II): Bacterial Catalysis. Geochimica et Cosmochimica Acta 46: 1073-1079.

Enander, L., Berghult, B. (1994) Increase of Alkalinity for Corrosion Prevention in Drinking Water Pipes. Vatten 50, 7-20

Graveland, A., Heertjes, P.M. (1975) Removal of Manganese from Ground Water by Heterogeneous Autocatalytic Oxidation. Trans. instn. chem. engrs. 53:154-164. J. AWWA 52:10:1326-1334.

Griffin, E.A. (1960) Significance and Removal of Manganese in Water Supplies.

Hallbeck, L. (1993) On the Biology of the Iron-oxidizing and Stark-forming Bacterium *Gallionella ferruginea*. Botaniska Institutionen. Göteborg. ISBN 91-86022-73-3.

Hallberg, R.O. (1988) Iron Oxidation in Groundwater - a Bacteriological or Chemical Process? (Oxidation av järn i grundvatten - en bakteriell eller kemisk process?) (in Swedish) Grundvattenförsörjning, Geohydrologi i praktiken) Symposium May 4 1988, VIAK AB and Svenska hydrologiska rådet, Stockholm p. 243-250.

Hamidi, A.A., Smith, P.G. (1992) The Influence of pH and Coarse Media on Manganese Precipitation from Water. Water Research 26:6:853-855.

Hatva, T., Niemistö, L., Seppänen, H. (1973) Examination and Removal of Iron in Ground Water. Aqua Fennica 3:82-94.

Hatva, T., Seppänen, A., Carlson, L. (1985) Removal of Iron and Manganese from Ground Water by Re-infiltration and Slow Sand Filtration. Aqua Fennica 15:2:211-225.

Hedberg, T. (1983) An Investigation of Alkaline Filter Materials.(Undersökning av alkaliska filtermassor.) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. publ. 6:83.

Hedberg, T. (1984). Alkaline Filter Materials and Acidic Well Water (Om alkaliska filter för sura brunnsvatten.) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. publ. 4:84.

Hemp, M.R. (1989) Iron Removal by Birm. Technical Report No. 89-WT-8. Clack Corporation, Windsor USA.

Horkeby, G. (1992) Filter Materials for the Neutralisation - an Investigation of their Properties for the Treatment of Acidic Well Water (Filtermassor för avsyrning - en undersökning av dess egenskaper för behandling av sura brunnsvatten) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Publ. 1:92.

Horkeby, G. (1992) Filter Materials for the Treatment of Acidic Well Water (Filtermassor för behandling av sura brunnsvatten) (in Swedish) Vatten 48, 292-297 Lund 1992.

Horkeby, G. (1993) Treatment Processes for the Removal of Iron and Manganese from Drinking Water. A literature reveiw (Järn- och manganavskiljningsmetoder för dricksvatten. En litteraturstudie) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Publ. 3:93

Horkeby, G., Björklund, L. (1995) Filter Materials for the Treatment of Acidic Well Water Containing Iron and Manganese - an Investigation of their Properties (Filtermassor för behandling av sura, järn- och manganhaltiga brunnsvatten - en undersökning av dess egenskaper) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Report 1995:2

Horkeby, G. (1995) Water Treatment Handbook for Acidic Well Water Containing Iron and Manganese (Handbok för behandling av sura järn- och manganhaltiga brunnsvatten) (in Swedish) Dept. of Sanitary Engineering, Chalmers University of Technology, Göteborg. Report 1995:3

Jönsson, L. (1984) Water Filter Construction (Vattenfilteranläggning.) (in Swedish) Patent nr. 8104667-4.

Knocke, W.R., van Benschoten, J.E., Kearney, M.J., Soborsk, A.W., Reckhow, D.A. (1990) Alternative Oxidants for the Removal of Iron and Manganese. Final report prepared for the AWWA Research Foundation, AWWARF, Denver Colorado.

Kronqvist, L., Sundlöv, B. (1991) Treatment Methods for Acidic Ground Water from Artesian Water Supply Wells. (in Swedish). P 6603 Källor, Swedish National Environmental Protection Board

Langelier, W.F. (1936) The Analytical Control of Anti-corrosion Water Treatment. J.AWWA 28, pp 1500-1521.

Letterman, R.D. (1993) Discussion: Pilot Testing a Limestone Contactor in British Columbia. J. AWWA 85, 2, p 91-92.

Letterman, R.D., Driscoll, C.T., Haddad, M., Hsu, H.A. (1986) Limestone Bed Contactors for Control of Corrosion at Small Water Utilities. Water Engineering Research Laboratory, Office of Research and Developement, U.S. Environmental Protection Agency, Cincinnaty, Ohio.

Letterman, R.D., Haddad, M., Driscoll, C.T. (1991) Limestone Contactors: Steady-state Design Relationships. Journal of Environmental Engineering, 117, No. 3, pp 339-358.

Lind Johansson, E., Hedberg, T., Berghult, B. (1994) Internal Corrosion of Copper Pipes for Drinking Water Supply. (in Swedish). Vatten 50,103-111.

Lindblad-Påsse, A. (1986) Problems with Iron Precipitation in Ground Water System Järnutfällningsproblem i grunvattensystem. (in Swedish) Dept. of Geology, Chalmers University of Technology, Göteborg. Publ. A53.

Meijers, A.P., Rook, J.J., Shultink, J.G.M.M., van der Laan, J., Poels, C.L.M. (1979) Objectives and Procedures for GAC Treatment. J. AWWA 71:11:628-637.

Mouchet, P. (1992) From conventional to Biological Removal of Iron and Manganese in France. J. AWWA 84:4:158-167.

National Swedish Food Administration (1989) Drinking Water Ordiance. National Food Administration, Uppsala (in Swedish). SLV, FS, 1989:30.

National Swedish Food Administration (1993) Drinking Water Ordiance. National Food Administration, Uppsala (in Swedish). SLV, FS, 1993:35.

Nealson K.H., Tebo, B. (1980) Structural Features of Manganese Precipitating Bacteria. Origins of Life 10:117-126.

O'Connor, J.T. (1971) Iron and Manganese. Water Quality and Treatment. Prepared and published by the American Water Works Association, McGraw-Hill Publishers, New York.

Olson, L.L., Twardowski, C.J. (1975) $FeCO_3$ vs $Fe(OH)_3$ Precipitation in Water Treatment Plants. J. AWWA 67:3:150-153.

Reijnen, G.K. (1976) Ontzuring van water met behulp van dolomitisch filtermaterial. Rijswijk (KIWA) Mededeling nr 47.

Reijnen, G.K. (1988) Ontzuren van grondwater. Nieuwegein (KIWA) Mededeling nr 101.

Robinson, L.R., Bredland, E.D. (feb. 1968) Removal of Iron and Manganese from Low Alkalinity Waters. Public Works 99:72-76.

Robinson, L.R., Dixon, R.J. (nov. 1968) Iron and Manganese Precipitation in Low Alkalinity Ground Waters. Water and Sewage Works 115:11:514-518.

Robinson, L.R., Summerford, C.R. (1970) Photosynthetic Difficulties in an Iron Removal Plant. Water and Sewage Works 117:9:311-318.

Sander, A., Elfström Broo, A., Berghult, B., Hedberg, T., Lind Johansson, E. (1996) The Influence of Water Quality on Corrosion of Iron and Copper Pipe Materials. Internal Corrosion in Water Distribution Systems. International Workshop and Seminar. Chalmers University of Technology, Göteborg, Sweden. May 22-24, 1995.

Shablovskaya, G.K., Zhumanov, O., Zabarilo, A.B.,Goronoskii, I.T. (1988) Removal of Manganese, Phosphates and Fluorides from Waters by Filtration through Semicalcined Dolomite. Sov. J. Water Chem. Technol. 10:3:116-118.

Sikora, J., Hansson, C-H., Ericsson, B. (1989) Pre-treatment and Desalination of Mine Drainage Water in a Pilot Plant. Desalination 75:363-378.

Souter, D. (1993) Eastfield Road, South Killingholme, Grimsby, South Humberside DN 40 3NF. (Personal discussions).

Stenström, T. (1995) Membrane Filtration Applied to Drinking Water Treatment (Membranmetoder för dricksvatten I) (in Swedish) National Food Administration. 24/95.

Stumm, W., Morgan, J.J. (1981) Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2:nd ed. Wiley Interscience.

Tillmans, J. et al (1912) Curve zur Ermittlung des für kalkangriffsfähigen Kohlensäureüberschusses. Ges.-Ing., 34:669.

van Dijk, J.C., Oomen, J. (1980) Design of the Dhahran Reverse Osmosis Treatment Plant. Proc. Int. Symp. Fresh Water Sea 7th 2:355-368.

van Dijk, J.C., Wilms, D.A. (1991) Water Treatment without Waste Material - Fundamentals and State of the Art of Pellet Softening. J. Water SRT - Aqua 40:5:263-280.

Vattenteknik AB, (1992) Water Treatment Processes (Vattenbehandlingsmetoder) (in Swedish) Malmö.

Viswanathan, M.N., Boettcher, B. (1991) Biological Removal of Iron from Ground Water. Water Science Technology 23:1437-1446.

Wong, J.M. (1984) Chlorination - Filtration for Iron and Manganese Removal. J. AWWA 76:1:76-79.