Paper 3

IRON AND MANGANESE IN WATER
Occurrence, drinking water standards, treatment options

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INTRODUCTION

Iron and manganese are commonly found in ground waters and some surface waters, such as lakes, that have a significant groundwater input. They are mostly present in the soluble reduced divalent form as ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions. The existence of dissolved iron and/or manganese in groundwater generally infers prior anaerobic conditions with the result that the water is likely to be devoid of oxygen and may also have a high carbon dioxide (CO_2) concentration. As well as being associated with groundwater input, the existence of dissolved iron and/or manganese in some deep lakes and reservoirs may be due to stratification, resulting in the development of anaerobic conditions in the bottom water zone and the dissolution of iron and manganese from floor deposits; the dissolved species are subsequently dispersed into the general water body by the annual overturn.

Waters containing iron and manganese in solution are clear and colourless. However, on exposure to air or oxygen, such waters become cloudy and turbid due to the oxidation of iron and manganese to the Fe^{3+} and Mn^{4+} states which form colloidal precipitates. The rates of oxidation are not rapid, and thus reduced forms can persist for some time in aerated waters (Sawyer & McCarty, 1967).

Dissolved iron and manganese may also form complexes with silica and naturally occurring humic substances. Such complexes may be difficult to oxidise and precipitate and hence to remove by conventional physico-chemical treatment.

The concentrations of iron and manganese in ground waters can vary widely but rarely exceed 5 mg/l. Although not a danger to health (refer following section), iron and manganese in drinking water at concentrations exceeding the recommended guideline values may give rise to a number of problems, including:

- Staining of kitchen and bathroom fittings
- Biofouling in distribution networks (causing taste and odour problems)
- Staining of laundry
- Fouling of heat exchangers and boilers
- Colour, turbidity and taste problems at high concentrations

DRINKING WATER STANDARDS

The current Irish Drinking Water Regulations (S.I. No. 278 of 2007) set the following limit values for iron and manganese:

	Limit value (µg/l)
Iron	200
Manganese	50

Iron and manganese are categorized as Indicator Parameters. The Indicator parameters largely comprise constituents that are considered not to be of critical health significance.

The WHO Guidelines for Drinking-water Quality (3rd. ed., 2006) do not set a limit value for iron in drinking water on the grounds that iron is not of health concern in the concentration range normally observed in drinking-water; taste and appearance of water are affected below the health-based value. The Guidelines set a health-related limit value of 0.4 mg/l for manganese. The latter value is derived on the basis of 20% of the total daily intake being of drinking-water origin. In the discussion of manganese, it is pointed out that:

- Manganese is an essential element for humans and other animals and occurs in many food sources; adverse effects can result from both deficiency and overexposure.
- Concentrations below 0.05-0.1 mg/l are usually acceptable to consumers but may sometimes still give rise to the deposition of black deposits in water mains over an extended period; this may vary with local circumstances.
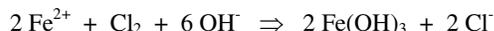
In the United States and Canada, iron and manganese in drinking water are considered as secondary contaminants that do not pose a danger to human health; the limit values are:

	Limit value (μg/l)
Iron	300
Manganese	50

REMOVAL METHODS

Where the permissible drinking water limit value for either Fe or Mn is exceeded in a water supply source, treatment is required to achieve compliance. The processes that are used for the removal of Fe and Mn invariably comprise two stages (a) an oxidation process in which the soluble forms of Fe and Mn are oxidized to form insoluble precipitates, and (b) a solid-separation process in which the precipitated material is removed from the water stream.

The oxidation process may be a direct chemical reaction, where the electron acceptor (oxidizing agent) may be oxygen or a strong oxidizing agent such as chlorine, chlorine dioxide, ozone, potassium permanganate. The oxidation/reduction reaction may be written as follows:

$$4\,Fe^{2+} \; + \; O_2 \; + \; 8\,OH^- \; + \; 2\,H_2O \; \Rightarrow \; 4\,Fe(OH)_3$$

$$2\,Fe^{2+} \; + \; Cl_2 \; + \; 6\,OH^- \; \Rightarrow \; 2\,Fe(OH)_3 \; + \; 2\,Cl^-$$

Alternatively, the precipitation reaction may be carried out in a biological process in which bacteria exert a rate-enhancing bio-catalytic effect on the oxidation reaction rate in the presence of dissolved oxygen. The associated bacteria include Gallionella, Leptothrix and Sphaerotilus, among others. Biologically mediated removal of iron and manganese has been shown to be an effective, economic and environmentally attractive method for the removal of iron and manganese, with many installations in operation worldwide (Mouchet, 1992; Hedberg, 1998, Sogaard et al., 2000, Williams, 2002). The typical process installation is a pressure filter or rapid gravity filter system, similar to that employed downstream of chemical coagulation in conventional surface water treatment. The process can be described as an attached film process, resulting in the accumulation of a biofilm/metal precipitate mixture that is removed by backwashing. Iron and manganese bacteria require different environmental conditions for optimal growth; hence, where biological removal of both iron and manganese is required, a 2-stage filtration process is generally necessary.

Whichever method of oxidation is employed, it is important that the ferrous iron concentration is reduced to near zero level as its presence in the supply system may give rise to biofilm growth on conduit surfaces.
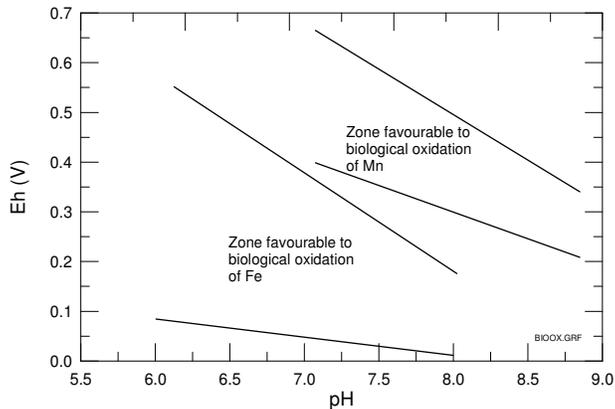
Biological removal of iron

The process infrastructure used for biological removal of iron is virtually the same as used in rapid gravity filtration. During filtration dissolved iron is converted to the insoluble ferric hydroxide species ($Fe(OH)_3$) that is retained within the filter voids and is intermittently removed by backwashing.

Oxidation-reduction potential (ORP, Eh) in conjunction with pH has been shown (Wolfe, 1964) to be of particular significance in identifying a growth environment favourable to iron bacteria, as shown in Fig 1 (Mouchet, 1992). It indicates that satisfactory operation of biological iron removal processes can be expected where the process pH is in the range 6.0 – 7.5 and where there is adequate dissolved oxygen (DO). In relation to the latter, it should be noted that DO saturation is not required; hence, simple cascade aeration of the raw water is generally sufficient to achieve the oxygen concentration required. For example, Viswanathan and Boucher (1991) reported a biological reduction in iron concentration from 2.6 mg/l to 0.1 mg/l at a process pH of 6.8 and a process Eh of 360 mV (the measured DO was in the range 5-6 mg/l). Tremblay et al. (1998) reported a biological reduction in iron concentration from 3.2 mg/l to 0.025 mg/l at a process pH of 5.7 and a process Eh of 500 mV (this performance was achieved at a low operating DO, in the range 0.2-0.6 mg/l).

The oxidation rate that can be achieved in biological iron removal processes is remarkable both in relation to the reaction rate and the mass of iron that can be oxidized. Sogaard et al (2001) reported the rate of biotic Fe precipitation/oxidation to be about 1000 times faster than previously found for abiotic physicochemical oxidation/precipitation. High filtration rates are applied, ranging from 10 to 30 m/h, depending on the raw water iron concentration. It is noted that the retention time in a 1m deep filter bed is less than 1 minute when operating at a filtration rate of 30 m/h. It would appear that biological oxidation of iron can be applied in direct filtration mode even at very high raw water iron concentrations (up to 20 mg/l).

The use of coarse filter media (effective size ≥0.8mm) allows a high filtration rate without incurring excessive head loss, while also providing capacity to retain precipitated ferric hydroxide.

Fig 1   **Growth environment for iron bacteria**

Water constituents that have an inhibitory effect on the biological removal of iron include H_2S and zinc (Mouchet, 1992). To avoid process retardation, the H_2S concentration should not exceed 0.01 mg/l. Iron removal rates of only 50% have been reported in the presence of zinc at 0.45 mg/l, with total inhibition of the treatment at a zinc concentration of 1 mg/l.

Based on the foregoing overview of the environmental conditions for the effective application of biological iron removal the most critical issue in practical application is likely to be the requirement for a near to neutral pH. In this regard it is noted that most Irish ground waters are in the hard, alkaline category. However, in many cases these waters also have a significant acidity (due to excess free carbon dioxide), which may reduce the pH to a near neutral value. Where biological iron removal is applied in these circumstances the aeration process used should be tailored to transfer sufficient oxygen into solution while at the same time minimizing the amount of carbon dioxide removed so as to avoid any significant increase in pH.

Biological removal of manganese

The process infrastructure used for biological removal of manganese is similar to that used for the biological removal of iron and is virtually the same as used in rapid gravity filtration. During filtration dissolved manganese is converted to the insoluble manganese dioxide (MnO_2) species that is retained within the filter voids and is intermittently removed by backwashing.

Fig 1 also shows the pH/Eh environment favourable to the growth of manganese bacteria. An alkaline pH in conjunction with a fully aerobic environment is required for implementation of biological manganese removal, typically a pH >7.5 and a DO concentration > 5 mg/l. Thus, the process environment required for biological removal of manganese differs from that required for the biological removal of iron; hence, it is generally not feasible to achieve a combined biological removal of both iron and manganese in the same biofilter.

As with biological iron removal, high filtration rates, in the range 10-30 m/h, can also be employed in the biological removal of manganese. High filtration head loss is avoided by using coarse filter medium with an effective size of 0.8-1.2mm.

All biological processes involve a start-up period during which the biomass required for process operation is built up. This seeding period for manganese removal has been found to be significantly longer than for iron removal and may extend up to 60 days.

Hedberg (1998) reported a successful upgrading of manganese removal at a waterworks through the replacement of a poorly operating permanganate chemical oxidation process by a biological process. The latter achieved a reduction in manganese concentration from raw water level of 0.4 mg/l to an effluent level of 0.02 mg/l at an operating pH of ca. 8.0.

As outlined in the foregoing sections, iron and manganese bacteria require different environmental conditions for optimal growth; hence, where biological removal of both iron and manganese is required, a 2-stage filtration process is generally necessary. The required intermediate treatment, following the first iron-removal stage, would typically involve raising the pH and the DO concentration to create optimal conditions for biological manganese removal (Williams, 2002). For waters that have a high degree of CO_2 super-saturation it may be possible to both raise the pH and DO by aeration, otherwise the addition of a strong alkali such as lime or sodium hydroxide may be required in addition to aeration.

Chemical precipitation of iron and manganese

Water containing dissolved iron and manganese is essentially chemically unstable in that precipitation of iron and manganese takes place on the uptake of oxygen when the water is aerated or exposed to atmospheric air. Various factors influence the rate of oxidation, as discussed in the following paragraph. The resulting precipitate tends to be colloidal in nature. Effective removal of iron and manganese by chemical precipitation requires the creation of a chemical environment conducive to rapid oxidation, the generation of removable precipitates and a process for precipitate removal.

The rate of chemical precipitation of iron and manganese is very much influenced by the pH/Eh environment. Referring to Fig 1, the lower boundaries of the pH/Eh zones conducive to the operation of chemical precipitation processes for iron and manganese removal roughly correspond to the upper boundaries for biological removal. Thus, removal of iron by chemical precipitation requires an alkaline pH and a highly aerobic environment. Similar conditions are required to achieve a satisfactory rate of oxidation of manganese with a pH >8. Oxidation is also enhanced by raising the Eh value through the use of strong oxidizing agents such as chlorine (Cl_2) or potassium permanganate ($KMnO_4$).

The stoichiometric dosing rates for the oxidation of iron and manganese using chlorine and potassium permanganate are:

Oxidant	mg/mg iron	mg/mg manganese
Chlorine	0.62	1.30
Potassium permanganate	0.91	1.92

Chemically precipitated iron and manganese are invariably removed in a rapid gravity or pressure filtration process. Special filter media, such as manganese greensand or silica sand coated with manganese dioxide are widely used to promote the oxidation process. It would appear that contact with the higher oxides of manganese on the filter medium exerts a catalytic effect on the oxidation of soluble iron and manganese. To maintain this catalytic effect it may be necessary to regenerate the MnO_2 coating by the intermittent use of $KMnO_4$. Greensand is typically used as the lower layer of a dual-media anthracite/greensand filter.

The factors that may inhibit the attainment of low residual iron and/or manganese concentrations by chemical precipitation include:

- Some of the dissolved iron may be sequestered by complexation with silica or humic substances, thereby retarding or preventing its oxidation.
- The natural pH of the water may be too low.

- The use of strong oxidants such as chlorine and potassium permanganate prevents any microbially generated oxidation.
- The colloidal nature of the chemical precipitates may lead to carryover in the treated water.

Filter back-washing

The accumulated deposits of iron and/or manganese in filters are removed by back-washing with a reverse flow of water or by a combination of water and air. The required frequency of back-washing is a function of the iron /manganese concentrations to be removed, the applied filtration rates and the filter media size. It is reported (Mouchet, 1992) that coarse media filters (>1mm) media, operated in a bio-oxidation mode, have a high retention capacity (1-5 kg Fe or Mn/m^2). Backwashing is typically initiated when the head loss across the filter has reached a set-point value. The set-point head loss should be at a value that provides a margin of safety against breakthrough of iron and/or manganese.

Efficient backwashing is absolutely essential to the maintenance of filter performance. An efficiently operating backwash system achieves the following goals (a) removes accumulated deposits from the filter bed, (b) maintains the media profile both in relation to materials and grain size distribution, (c) does not cause a loss of media from the bed through either washout or migration downwards into the under-drain system, and (d) restores the clean bed filter head loss.

Other processes

Attempts have been made to sequester dissolved iron and manganese by the addition sequestering agents such as polyphosphates or silicates in conjunction with chlorine. There is a lack of research data on these processes, which appear to have met with limited success (AWWA, 1987).

Iron and manganese in true solution can also be removed by ion exchange. This method may be appropriate for use on a domestic scale, where it might be used in conjunction with water softening.

SUMMARY

Concentrations of iron and manganese in excess of the recommended permissible limits for drinking water are commonly found in ground waters and may also occur intermittently in some lake and reservoir waters. While these solutes are not damaging to health, their precipitation adversely affects the aesthetic quality of water supplies and may be a source of nuisance to consumers.

The process effectiveness of biochemical oxidation for the removal of iron and manganese has been reliably demonstrated in water supply practice in a number of countries. Reliable process performance requires an appropriate chemical environment. In this regard, it should be noted that the optimal pH/Eh environment for iron bacteria differs from that for manganese bacteria. Hence, where removal of both iron and manganese is required, a 2-stage process is generally necessary for biochemical removal. Thus, where the raw water chemistry is supportive of biochemical oxidation, it should normally be evaluated as a first treatment option, as it has the potential to be the most economically and environmentally attractive solution in that no chemical additions are likely to be required and reaction rates are quite rapid, requiring a relatively small process reactor volume. Where possible, a pilot plant study should be carried out as part of the design process both to verify feasibility and also to assess the likely duration of the seeding period necessary to establish the process. The latter is of particular significance in relation to biological manganese removal.

The removal of iron and manganese by a combination of chemical oxidation/rapid filtration has been widely used in water supply practice over a long period of time. The oxidation step may be carried out by aeration or more usually by use of a strong oxidant such as chlorine or, where manganese removal is required, by potassium permanganate. For manganese removal, a greensand filter medium may be used to enhance the rate of oxidation of the dissolved manganese species to MnO_2. It may be necessary to intermittently dose $KMnO_4$ to maintain the catalytic properties of the greensand medium. The rate of chemical precipitation of iron and manganese is highly dependent on pH and also requires a highly aerobic environment.

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