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Biological and Physico-Chemical Removal of Iron from Potable Waters

Redox Potential as an Indicator of Treatment Effectiveness

By

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Master of Engineering.

ABSTRACT

The first objective of this research was to evaluate oxidation-reduction potential (ORP) as an indicator of effective iron removal in a biological process and to determine its relationship to dissolved oxygen (DO) and residual iron in the filtered water. Biological removal of iron to produce drinking water was established on one full-scale and two pilot-scale plants at two sites in France. Results show that below a minimum DO concentration of approximately 0.3 mg/L, residual iron concentration was related to ORP in the filtered water. Above the minimum DO requirement, ORP on the order of approximately 500 mV consistently reflected effective iron treatment and residual iron concentrations less than the French norm for potable water of 0.2 mg/L.

Secondly, two catalytic materials of filtration known as *Ferrolite MC2* and *Purolite* were investigated on pilot-scale for their capacity to oxidize iron and manganese. Results showed that both materials eliminated dissolved iron to below detection levels regardless of DO or filtration rates up to 15 m/h (*Ferrolite MC2*) and 20 m/h (*Purolite*). During the trial period where no filter regeneration was carried out, the elimination of dissolved iron and dissolved manganese, respectively, were 100% and 77% for *Purolite* and 100% and 65% for *Ferrolite MC2* for a raw water with 3.47 mg/L of dissolved iron and 0.317 of dissolved manganese. *Purolite* filtered a total volume of 1127 L or 137 L/kg of catalytic material and *Ferrolite MC2* filtered a total of 1457 L or 217 L/kg.

RÉSUMÉ

Le premier objectif de ce travail était d'évaluer l'emploi du potentiel d'oxydo-réduction (potentiel redox) comme indicateur de déferrisation par un procédé de déferrisation biologique et d'établir un rapport entre le potentiel redox et l'oxygène dissous (OD) ainsi qu'avec la concentration de fer résiduel dans l'eau filtrée. Un procédé industriel de production d'eau potable et deux procédés pilotes ont été utilisés à deux endroits différents en France. Les résultats indiquent que, lorsque l'OD est inférieure à 0,3 mg/L, la concentration en fer résiduel dans l'eau filtrée est liée au potentiel redox de l'eau. Aux concentrations d'oxygène dissous supérieures à cette valeur seuil, le potentiel redox demeurait constant à plus de 500 mV et indiquait une élimination satisfaisante du fer et des concentrations en fer résiduel inférieures à la norme française de 0,2 mg/L.

Deuxièmement, deux matériaux filtrants catalytiques, la *Ferrolite MC2* et la *Purolite*, ont été étudiés en pilote pour établir leur capacité d'oxydation du fer et du manganèse. Aux concentrations en oxygène dissous étudiées et à des vitesses de filtration jusqu'à 15 m/h (sur *Ferrolite MC2*) et 20 m/h (sur *Purolite*), la concentration de fer dissous résiduel est demeurée inférieure au seuil de détection pour les deux matériaux. Durant toute la durée des essais et sans aucune régénération des filtres, les rendements d'élimination du fer et du manganèse ont été respectivement de 100% et de 77% pour la *Purolite* et de 100% et 65% pour la *Ferrolite MC2*, pour une eau brute contenant 3.47 mg/L de fer dissous et 0.317 mg/L de manganèse dissous. Les volumes d'eau filtrée ont été respectivement de 1127 L ou de 137 L par kg de matériau catalytique pour la *Purolite* et de 1457 L ou 217 L par kg pour la *Ferrolite MC2*.

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DO	=	dissolved oxygen
DRI	=	dissolved residual iron
DRM	=	dissolved residual manganese
ORP	=	oxidation reduction potential
TRI	=	total residual iron
TRM	=	total residual manganese

1. INTRODUCTION

The presence of reduced forms of iron and manganese in groundwater is a natural phenomenon, particularly in acidic waters. Concentrations generally found in natural waters do not have toxicological significance (Lehr et al., 1980). However, when these groundwaters are tapped for potable water, reduced ions come into contact with oxygen and are precipitated as red or black insoluble oxides. These precipitates can lead to corrosion and obstructions in underground water canals, and problems for the consumer, such as tinted, metallic-tasting drinking water (Lehr et al., 1980). Dissolved iron and manganese ions are also a nuisance for industries which rely on clear water, such as the food industry and the pulp and paper industry (Lehr et al., 1980).

Therefore, in groundwater that is destined for drinking water production, the level of iron is regulated based on aesthetic and taste considerations, rather than concern over physiological effects (Lehr et al., 1980). French regulation indicates maximum admissible concentrations of 0.2 mg/L and 0.05 mg/L for iron and manganese, respectively (Degrémont, 1991). Canadian water quality guidelines indicate maximum allowable concentrations of 0.3 mg/L for iron and 0.05 mg/L for manganese (Health Canada, 1996).

Treatment of iron and manganese can be accomplished by either physico-chemical means, which includes the use of catalytic materials, or by biological means. In the case of a conventional physico-chemical process, the precipitation is induced by an intensive aeration, usually followed by the addition of a chemical oxidant (in the case of manganese), and then filtration on a sand filter. In the catalytic process, the filtration

material is, for example, a specially coated sand or ceramic material which catalyzes the oxidation. Biological treatment makes use of specific micro-organisms which instigate the oxidation of reduced forms of iron and manganese in raw water, and also act to retain the precipitates in the biological sand filter.

The primary objective of this research is to investigate oxidation-reduction potential (ORP or redox potential) as an indicator of biological iron treatment effectiveness. This is accomplished by evaluating the impact of dissolved oxygen concentration (DO) on the iron removal process and then determining the relationship between ORP and DO and between ORP and the residual iron concentration in the filtered water. ORP has been widely studied for application in control of biological wastewater treatment systems (Charpentier et al., 1987; Wareham et al., 1993). Biological drinking water treatment is similar in that specific bacteria mediate the presence of reduced and oxidized species (i.e. iron) which in turn impact upon the ORP.

The second objective of the research is to evaluate iron and manganese oxidation on two granular catalytic materials known as *Purolite* and *Ferrolite MC2*. Each material is studied on pilot-scale at different velocities of filtration and at various DO levels. The performance of each is evaluated by the volume of raw water filtered per unit mass of material for given residual concentrations of iron and manganese. These two materials were selected after they were studied as part of previous unpublished research (Thill, 1995) through the International Center for Research on Water and the Environment (Centre International de Recherche Sur l'Eau et l'Environnement or C.I.R.S.E.E.) which evaluated several prevalent catalytic materials for their effectiveness with respect to iron and manganese treatment. *Ferrolite MC2* is selected for the current study as it was found

to achieve the best overall performance of the materials tested. *Purolite* is reconsidered as it was shown to be the material most widely used in the full-scale treatment of iron and manganese.

Although the research may demonstrate a promising application of ORP as an indicator in biological treatment of iron, it should be noted that raw water conditions vary greatly from installation to installation, making the operating conditions at different treatment facilities quite diverse. Pilot-scale studies are required to determine the importance of ORP for any specific application. Similarly, full-scale use of a catalytic material of filtration such as *Purolite* or *Ferrolite MC2* must first be verified on a pilot-scale under site-specific conditions. Therefore, the current work simply provides an example as to how ORP can be evaluated as an indicator in biological treatment and the aforementioned catalytic materials can be evaluated for iron and/or manganese oxidation under a particular set of conditions.

2. LITERATURE REVIEW

2.1 Chemical Characteristics of Iron and Manganese

Iron is the fourth most abundant element on the earth's surface (Stolzenberg, 1995), while manganese is twelfth (Pisarczyk, 1995). Surface water usually contains only precipitated forms of iron and manganese and they are easily removed by simple clarification. The presence of reduced iron and manganese is then generally reserved for deep groundwater sources, where the water table is deprived of oxygen and is in contact with minerals which contain iron and manganese (Lehr et al., 1980). These two elements are frequently found together in groundwater sources, but there have been cases where only one or the other is present in high concentration (Degrémont, 1991).

To properly specify a method of treatment for the selected groundwater source, it is important to identify several parameters of the raw water, in addition to concentrations of total and dissolved iron and manganese. The measure of pH, alkalinity, hardness, redox potential, colour, organic matter, silicates, phosphates, chlorides, sulfates, turbidity, ammonia, nitrates, dissolved oxygen, carbon dioxide and hydrogen sulfide are analyses of significant importance (Degrémont, 1991). Many parameters need to be identified on site to avoid alteration of chemical species upon contact of the groundwater with air.

2.1.1 Iron

Elementary iron exists in either of two reduced states: ferric iron (trivalent) which is represented by Fe^{3+} and ferrous iron (divalent), represented by Fe^{2+} (Stolzenberg, 1995). Figure 1 presents the forms of iron found in natural water sources.

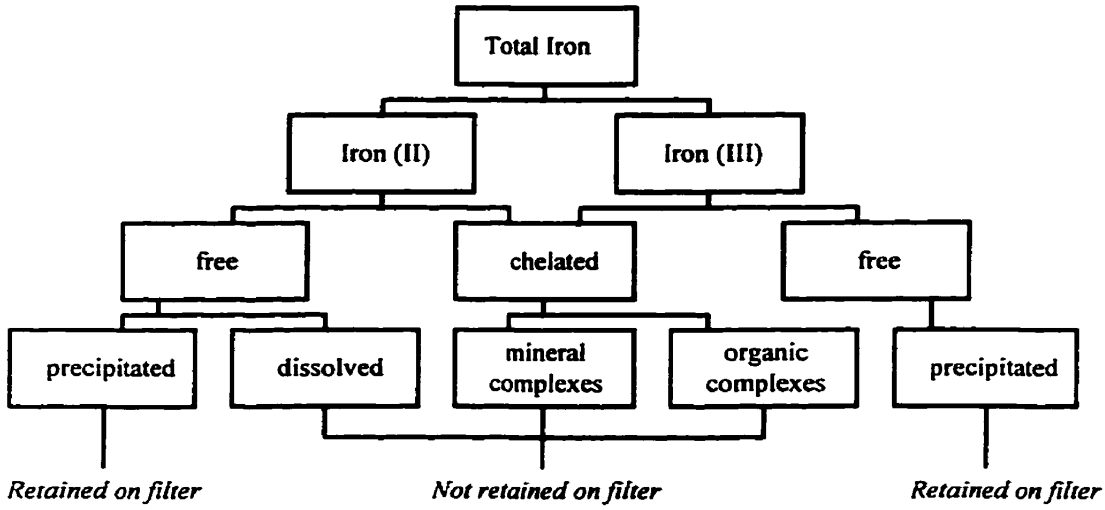

Figure 1. The states of iron (after Degrémont, 1991).

The presence of chelated iron can complicate removal, but only when conventional physico-chemical methods are employed (Mouchet, 1992). Hence, when considering this treatment, it is important to be able to differentiate between the forms of iron not retained on a filter. A method to determine the amount of iron not retained which is bound with complexing agents is well documented (Degrémont, 1991). Examples of chelating agents which have been found to associate with ferrous and ferric iron are minerals (silicates, phosphates, polyphosphates, cyanates, or sulfides) and organics (humic, fulvic or tannic acids) (Degrémont, 1991; Mouchet, 1992).

Figure 2 illustrates the importance of pH and redox potential with respect to the states of iron in aqueous solution. It should be noted that this figure applies for aqueous systems in which no interference is presented by chelating agents. It can be easily verified from Figure 2 that in a mildly acidic, reducing environment (absence of oxygen),

iron is generally stable, in dissolved ferrous ion form (Stolzenberg, 1995). Also, Figure 2 shows that ferric iron exists in dissolved form only for very low values of pH.

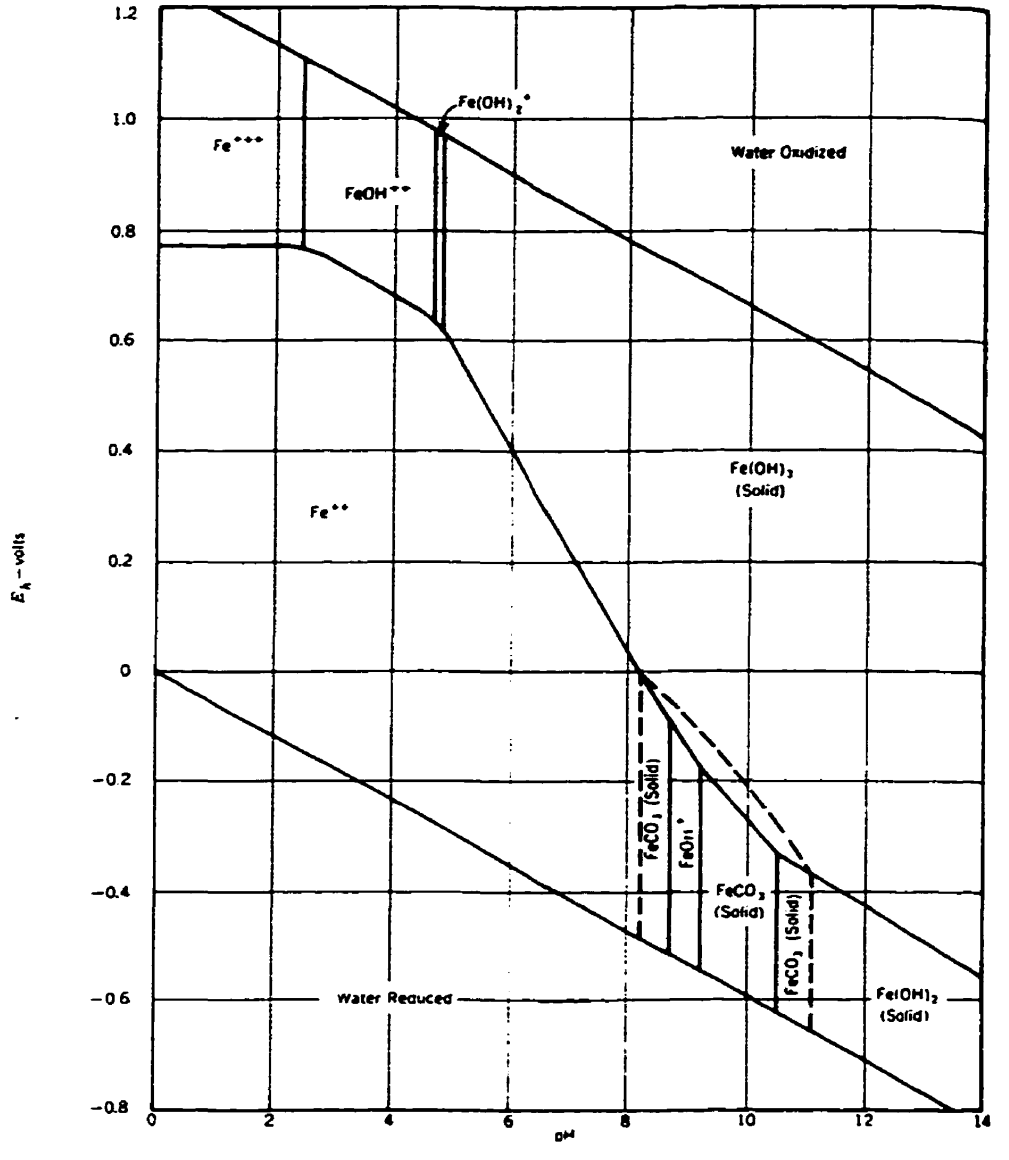

Figure 2. pH-potential diagram for iron (from Hem, 1961).

Within a normal aquatic pH range (slightly acidic to slightly basic), a slow oxidation of Fe^{2+} to Fe^{3+} takes place with increasing redox potential (dissolution of oxygen). The oxidation rate increases with pH and precipitation of ferric hydroxide ($Fe(OH)_3$) results (Droste, 1997).

The lower right hand corner of Figure 2 indicates other important compounds which can arise in the iron-aquatic system. Ferric carbonate or ferric hydroxide species will occur in the absence of oxygen and at high pH and their appearance is dependent on the carbonate content of the water (Stolzenberg, 1995). Carbonate species activity equivalent to either 100 ppm or 1000 ppm as bicarbonate are represented by the solid boundaries or dashed boundaries, respectively. As the pH is increased further, the ferrous ions form stable hydroxide precipitates (Hem, 1961).

2.1.2 Manganese

The element manganese exists in oxidation states ranging from -3 to +7 (Pisarczyk, 1995). The ion with an oxidation state of +7 is chemically produced and is very important commercially in the formation of the permanganate ion, MnO_4^-, an extremely powerful oxidizing agent. As will be shown later, potassium permanganate is often used in the chemical oxidation of iron and manganese in physico-chemical treatment plants.

In deep ground water sources, the divalent form, manganous ion Mn^{2+}, is found to be stable in solution up to a pH of about 8 or 9. This behaviour is represented in Figure 3, a diagram for manganese which is analogous to Figure 2 for iron.

Figure 3 shows that $Mn(OH)_2$ is produced in the absence of oxygen when the pH rises above about 8.3 (Pisarczyk, 1995). Trivalent and mixed valent manganese

compounds (Mn_2O_3 and Mn_3O_4, respectively) will result under mildly oxidizing conditions. When the pH is further increased into the range 9 - 10 and redox potential between 500 and 600 mV, Mn^{2+} and Mn^{3+} are oxidized to manganese (IV) which readily precipitates as MnO_2.

Manganese (IV) dioxide is of special interest for its surface characteristics, which make it capable of adsorbing charged species. This characteristic is relevant to catalytic materials used to eliminate iron and manganese, as will be discussed in Section 2.2.4.

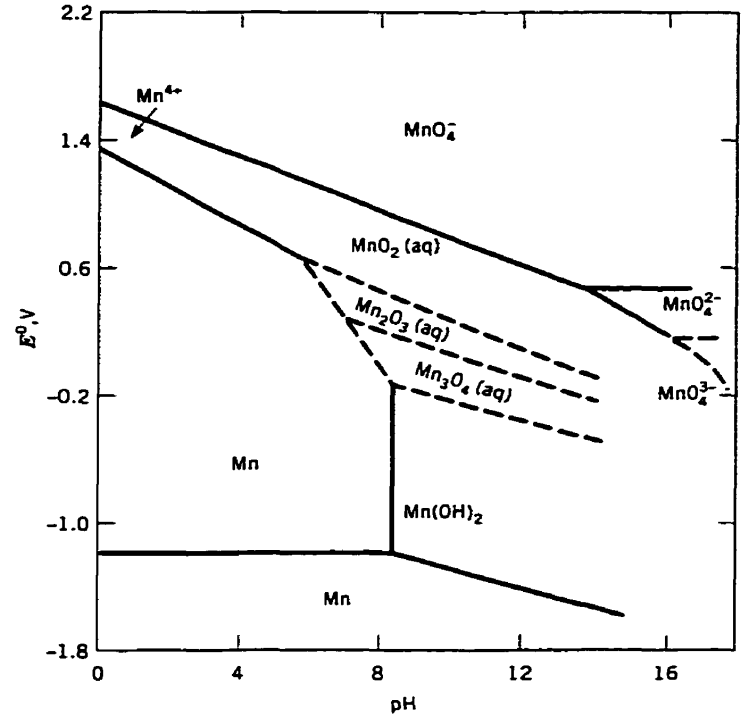

Figure 3. pH-potential diagram for manganese (from Pisarczyk, 1995).

2.2 PHYSICO-CHEMICAL TREATMENT

The classical physico-chemical approach to iron and manganese removal is known as conventional treatment (Mouchet, 1992). The more recent developments in the realm of physico-chemical treatments include the use of catalytic materials of filtration.

Basic iron removal from water with the conventional approach can be achieved through aeration followed by filtration. Figure 2 illustrates the behaviour of iron species in such a system. Treatment becomes more complicated when complexed forms of iron or iron concentrations above 5 mg/L are detected, and when manganese is present in high concentrations (Degrémont, 1991).

2.2.1 Aeration

In the removal of iron from ground water, it is always advantageous to carry out an aeration as the first stage, even if a chemical oxidant is required further on. The aeration step allows for savings on costly chemical oxidants because the easily oxidized species are already precipitated. In addition, efficient aeration permits an adequate concentration of dissolved oxygen for the final product (Degrémont, 1991).

Aeration is carried out either under pressure in an oxidation contact tower or at atmospheric pressure. Atmospheric installations include trickling over cascades or over contact media (with or without air circulation), open air spraying, diffused aeration or mechanical aeration with turbines (Droste, 1997).

The pressurized installations are advantageous when the treatment plant operates under the back pressure in the water distribution network. But open aeration is also useful for the elimination of dissolved carbon dioxide and hydrogen sulfide gases. If the carbon dioxide concentration is high and cannot be removed in open aeration, costly neutralization may be necessary.

The oxidation of ferrous iron by elemental oxygen is expressed by the following equation (Droste, 1997):

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \quad (1)$$

It has been experimentally determined that a pH of at least 7 is required to achieve effective oxidation of iron by elemental oxygen (Degrémont, 1991; Mouchet, 1992). Since many raw ground waters are mildly acidic, a pH adjustment by addition of lime or caustic soda is sometimes necessary (Degrémont, 1991).

2.2.2 Chemical oxidation

Ordinarily, if manganese is present in high concentrations along with iron in raw water, it will not precipitate following simple aeration (Degrémont, 1991). As shown in Figure 3, a much higher pH is required for manganese to be oxidized with oxygen than for iron. Thus the addition of a chemical oxidant becomes a necessary step to achieve efficient manganese removal.

High concentrations of iron and the presence of complexed forms of iron also require the use of chemical oxidizing agents. Oxidants such as chlorine dioxide (ClO_2) and potassium permanganate ($KMnO_4$) are used to provoke the oxidation of iron and manganese. Ozone is also used in the treatment of manganese. These chemical oxidations are illustrated by the following reactions (Droste, 1997; Degrémont, 1991):

$$2Fe^{2+} + Cl_2 + 6H_2O \rightarrow 2Fe(OH)_3 + 6H^+ + 2Cl^- \quad (2)$$

$$3Fe^{2+} + MnO_4^- + 5OH^- + 2H_2O \rightarrow 3Fe(OH)_3 + MnO_2 \quad (3)$$

$$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2 + 2O_2 + 2Cl^- + 4H^+ \quad (4)$$

$$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+ \quad (5)$$

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (6)$$

With the use of chemical oxidants, a contact basin is often employed to improve oxidation efficiency. In addition, coagulants and flocculants are sometimes added to facilitate removal of fine precipitates. Finally, with high levels of iron or manganese to be removed and/or the presence of complexed forms of iron or manganese, a decantation stage may be necessary (Degrémont, 1991).

As an alternative to chemical precipitation of iron and manganese compounds, sequestering agents such as sodium silicates, phosphates or polyphosphates are added to water. These bind with iron and manganese in polymeric colloidal complexes and inhibit them from forming colour or turbidity in the water distribution network (Droste, 1997).

2.2.3 Filtration

Operating conditions for filtration are likely to vary significantly from one installation to another, due to different precipitates which arise from the various previous stages (Mouchet, 1992).

In the case of classic sand filters, the effective size of the sand particles ranges from 0.5 to 1 mm and the rate of filtration between 5 and 15 m/h. The quantity of iron retained on the filter is typically between 0.2 and 1.2 kg iron per m^2 (cross sectional area of the filter). Head loss is generally on the order of 60 kPa. Crushed anthracite (hard coals) has also been used as filter material and in combination with sand in bi-layer filters (Degrémont, 1991).

At the end of the iron removal process, disinfection is necessary (generally with chlorine), to eliminate any bacteria, including the iron bacteria, which are often present in

the raw water. These latter micro-organisms are known to obstruct pipelines and cause corrosion (Droste, 1997; Degrémont, 1991).

A backwash using treated or raw water and air scour is the primary form of maintenance for physico-chemical filters.

In brief summary, conventional physico-chemical treatments are generally reliable methods of elimination for iron and/or manganese. After many years of use, their most favorable conditions are well known, which assures their continued successful application (Mouchet, 1992).

2.2.4 Filtration on catalytic materials

From within the realm of physico-chemical treatments of iron and manganese has emerged the use of specially prepared materials of filtration. According to Cole (1986), iron and manganese removal by catalytic materials is a known reliable method of treatment in North America.

These filters generally consist of a material which naturally contains manganese (IV) dioxide, or a material artificially coated with it. As discussed earlier, MnO_2 has been studied for its amphoteric nature and ability to partake in surface - solution exchanges of hydrogen and hydroxide ions (Pisarczyk, 1995). According to Stumm and Morgan (1996), the surface charge of the hydrous MnO_2 particle in a packed filter is negative above a pH of about 5. Thus it has an outer layer of exposed OH^- groups capable of adsorbing charged species such as H^+ and metal ions. Figure 4 illustrates this phenomenon.

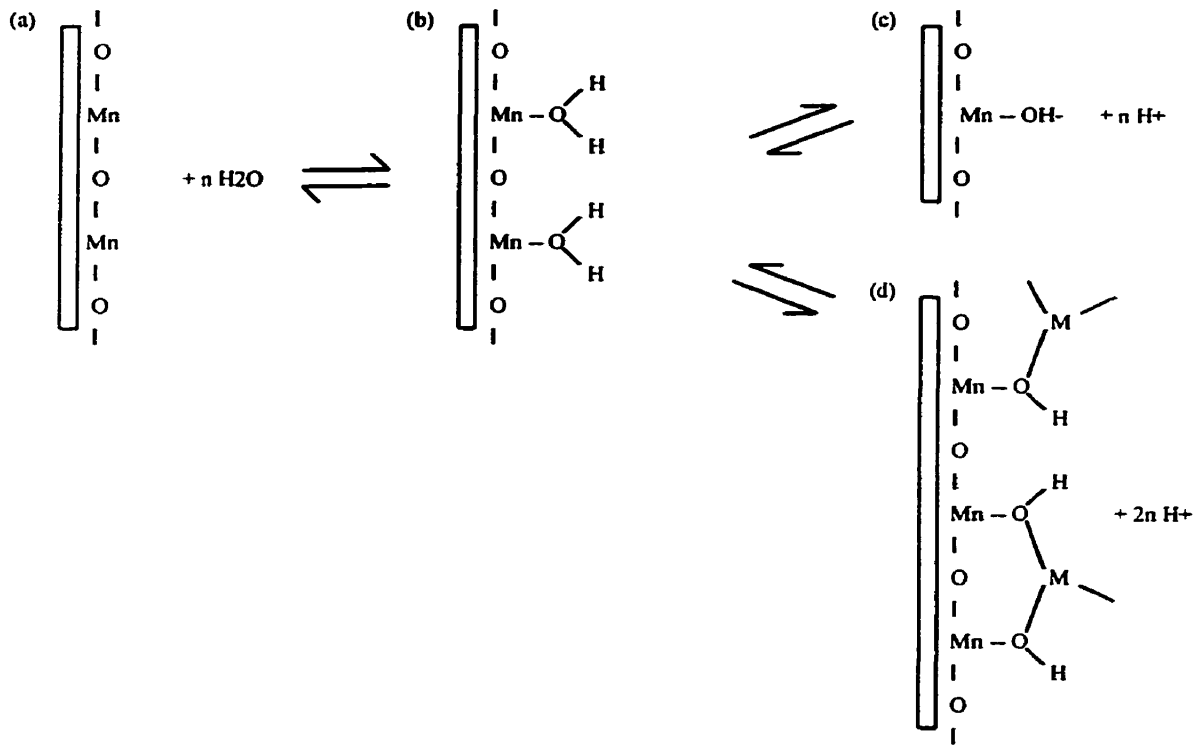

Figure 4. Adsorption of metal ions on hydrous manganese (IV) dioxide (after Pisarczyk, 1995). (a) catalytic material (b) hydration of MnO_2 (c) surface-solution exchanges with H^+ (d) surface-solution exchanges with metal cations, represented by 'M'.

Following adsorption, catalytic oxidation of the metal ions takes place while the local surface manganese dioxide is reduced. The sorption/oxidation mechanism for iron and manganese can be expressed by the following equations:

$$2Fe^{2+} + 2MnO_2 + 4OH^- + H_2O \rightarrow 2Fe(OH)_3 + Mn_2O_3 \quad (7)$$

$$Mn^{2+} + MnO_2 + H_2O \rightarrow Mn_2O_3 + 2H^+ \quad (8)$$

After a certain time of operation, the filter becomes saturated and needs to be regenerated by a solution of permanganate, as shown by the following reaction:

$$3Mn_2O_3 + 2MnO_4^- + H_2O \rightarrow 8MnO_2 + 2OH^- \quad (9)$$

Several different catalytic materials exist on the market, but only *Purolite* and *Ferrolite MC2* are considered in this study. The selection of these two materials was based primarily on previous related research described in an unpublished report (Thill, 1995). Thill (1995) used several pilot columns which were assembled in parallel, each capable of operating independently of the others. Gravitational filtration on each material was studied without the use of reagents or an air injection. The cross sectional area and bed depth of each pilot was 0.002 m^2 and 1 m, respectively. Average raw water conditions included a pH of 7.1, Eh of 175 mV, DO content of 0.8 mg/L, total iron content of 1.65 mg/L and total manganese content of 0.115 mg/L.

2.2.4.1 Purolite

Purolite is a trade name for a greensand which has been artificially coated with a layer of manganese (IV) dioxide. Greensand is a granular, naturally occurring zeolite, with the mineral composition $(K,Na,Ca)_{1.2-2}-(Fe^{3+},Al,Fe,Mg)_4Si_{7-7.6}Al_{1-1.4}O_2(OH)_4 \cdot nH_2O$ (Droste, 1997). Purolite is generally used alone as the material of filtration (not in combination with sand). Thill's (1995) results for the pilot plants described above show that Purolite was effective at removing 100% of the iron and 95% of the manganese for slow rates of filtration in the range of 1 - 3 m/h. For elevated rates of filtration (7 m/h), iron removal was still nearly 100% but only up to 30% of manganese was eliminated.

2.2.4.2 Ferrolite MC2

Ferrolite MC2 consists of a granular ceramic medium which, like Purolite, is coated with MnO_2. Thill (1995) showed Ferrolite MC2 to behave as well as Purolite with respect to iron elimination, and at higher velocities of filtration (13 and 24 m/h). It was observed

that for iron removal to below the detection limit, ORP was consistently greater than 500 mV. Ferrolite MC2 also performed well for manganese removal at the lower flow rate and removed up to 75% of the manganese at the higher flow rates. In terms of manganese elimination, Thill (1995) showed that Ferrolite MC2 filtered approximately 280 L or 42 L/kg before requiring regeneration.

Thus these two materials seem to be promising alternatives to conventional physico-chemical treatment. However, their reliability must be evaluated for a specific application, which forms the second part of this study.

2.3 Biological Treatment

For many years physico-chemical treatment was considered to be the only reliable method to effectively rid drinking water of high iron and manganese concentrations (Mouchet, 1992). In the United States, investigations of conventional treatment plants revealed that up to 40% of installations were not eliminating enough iron (Robinson et al., 1987; Andersen et al., 1973). Similarly in France in the 1970s, it was found that only two-thirds of conventional plants were achieving sufficient removal of iron and manganese (Mouchet, 1992). On the other hand, certain installations were performing adequately even if their operating conditions were not favourable to effective physico-chemical elimination (Mouchet, 1992). In these latter cases, massive developments of iron and manganese bacteria were discovered in the sludge from the backwash and determined to be the cause of the satisfactory removal. Thus biological treatment, previously thought to be ineffective, came to the forefront of new studies in the elimination of iron and manganese (Hettler, 1982; Viswanathan et al., 1991).

2.3.1 Iron bacteria

These microorganisms are ubiquitous in the environment, being found not only in ground water, water treatment facilities and raw and treated water canals, but also in spring water, marshes, ponds, lake sediment, mines and various soils (Degrémont, 1991). Although many iron bacteria are also associated with manganese, the present work is concerned only with iron removal by biological means. Thus, the bacterial characteristics discussed will focus primarily on iron bacteria. For simplicity, the designation "iron bacteria" encompasses the bacteria which may elsewhere be differentiated as either iron-oxidizing or iron-accumulating bacteria (Ehrlich, 1990).

Table 1 indicates the bacteria of interest, which are sessile (fixed growth) microorganisms. They include filamentous ('sheathed') bacteria (i.e. *Leptothrix*), stalked bacteria (i.e. *Gallionella*) and encapsulated bacteria (i.e. *Sidercapsa*).

Table 1. Some iron bacteria.

Order	Family	Genus	Observations
Chlamydobacteriales	Chlamydobacteriaceae Crenothricaceae	*Leptothrix, Sphaerotilus* *Crenothrix, Clonothrix*	Filamentous; Fe/Mn deposits; heterotrophic or facultatively autotrophic
	Siderocapsaceae	*Siderocapsa, Siderobacter, Sideromonas, Naumanniella, Ochrobium, Sidercoccus*	Encapsulated; Fe/Mn deposits; heterotrophic
Caulobacteriales	Gallionellaceae	*Gallionella*	Stalked; Fe deposits; autotrophic

In general, iron bacteria can be distinguished by their morphology (Degrémont, 1991). While the filamentous and stalked bacteria are easily identified under microscope, the Siderocapsaceae family of bacteria are difficult to detect upon direct examination due to their rods or cocci cells which become covered in iron precipitates (Mouchet, 1992). Figures 5 and 6 show the characteristic forms of species *Leptothrix ochracea* and *Gallionella ferruginea*, respectively. Figure 7 presents the typical *Sidercapsa treubii.*

Leptothrix spp. take the form of small rods in chain-like formation (a trichome), enclosed in a sheath in which iron precipitates are deposited (Mulder and Deinema, 1981). *Gallionella* consists of a vibrioid (bean-shaped) cell from which a fibrillar stalk is excreted on the concave side. The long and twisted stalk becomes heavily encrusted with ferric hydroxide and is the most distinct feature in Figure 6 (Hanert, 1981a).

The genus *Metallogenium*, of most significance in the oxidation and accumulation of manganese, is also capable of accumulating iron oxides, which make it relevant in the present study (Zavarin, 1981). Some authors have linked *Metallogenium* with the Siderocapsaceae family (Mouchet, 1992) and others with the appendaged (stalked) and budding bacteria (Staley et al., 1981). At a certain stage *Metallogenium* is a coccoid, from which cocci sprout by radial filaments, giving the organism a characteristic "star" shape, as shown in Figure 8. Deposits of manganese over time lead to encrustation of the colony, which can appear as an amorphous lump (Zavarin, 1981). Like Siderocapsaceae microorganisms, *Metallogenium spp.* may resemble some precipitates, making them difficult to clearly identify (Ehrlich, 1990). *Metallogenium* is reportedly heterotrophic, but may also be facultatively autotrophic (Ehrlich, 1990).

(a) (b)

Figure 5. *Leptothrix ochracea* (a) cells moving out of sheaths and forming new sheaths (b) broken old sheaths covered and impregnated with ferric hydroxide in slowly running iron (II)-containing soil extract (from Mulder and Deinema, 1981). Bar = 10 μm.

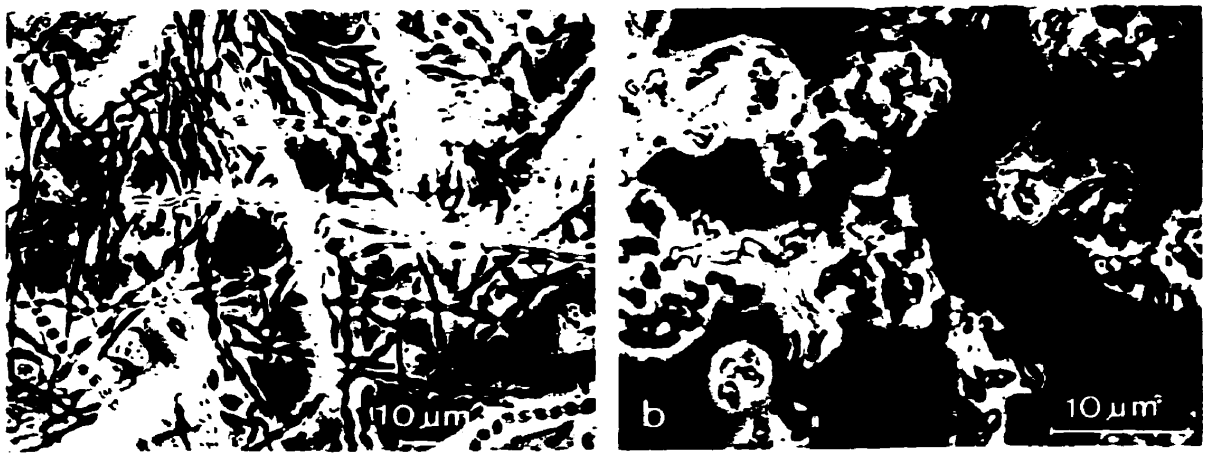

Figure 6. *Gallionella ferruginea* (a) extremely pure deposit in drainage line near the groundwater table (b) heavy iron-coated stalks (from Hanert, 1981a).

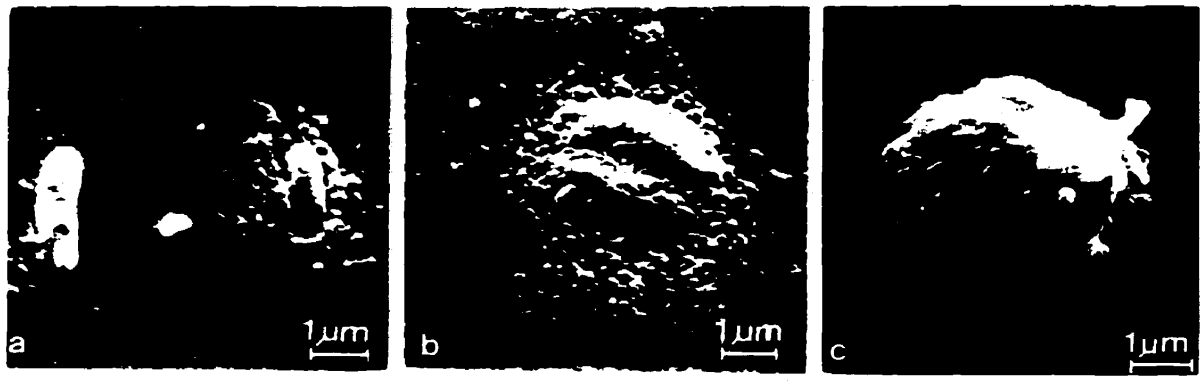

Figure 7. *Sidercapsa treubii* slide ongrowth in aquarium-natural water culture (a) single cells at the initial phase of capsule formation (b) two cells coated with slime and iron particles (c) slime capsule completely coating cell (from Hanert, 1981b).

Figure 8. *Metallogenium* with buds and daughter colonies from lakes (arrow) (× 10 000) showing excretions of iron and manganese hydroxides (from Rheinheimer, 1992).

Nearly all the species described in Table 1 are found to accumulate both iron and manganese (Hanert, 1981b; Mulder and Deinema, 1981). Only *Gallionella* is thought to accumulate iron alone (Hanert, 1981a). The mechanisms of oxidation and/or accumulation are discussed in the following section.

2.3.2 Mechanism for bacterial iron uptake

All iron bacteria are aerobic or microaerophilic, meaning that they require oxygen; and chemotrophs, meaning they obtain required energy through enzymatic oxidation of organic or inorganic matter (chemosynthesis) in their environment. The energy is subsequently used to assimilate their source of carbon. which can either come from organic (heterotrophs) or inorganic (autotrophs) material (Droste, 1997).

The concept of autotrophy was first proposed by Winogradsky in 1888 (Starkey, 1945), following studies on sulfur bacteria. Winogradsky concluded that iron bacteria had similar physiology, using iron oxidation as a source of energy. He proposed the following mechanism: the iron bacterium oxidizes ferrous iron inside its cell, ferric hydrate is precipitated outside of the cell, and energy is used to assimilate the carbon in carbon dioxide (Starkey, 1945).

As referenced in Viswanathan and Boettcher (1991), Temple and Colmer (1951) accounted for the efficiency of carbon assimilation and the fact that iron oxidation does not release much energy in their estimation that obligate aerobes require 577 moles of ferrous iron per mole of carbon. This finding may explain why biological iron removal facilities tend to function well at high flow rates (Mouchet, 1992).

The microorganism *Gallionella* is thought to be the only strict autotroph (Wolfe, 1958; Rheinheimer, 1992), as mentioned in Table 1. Although enzymatic oxidation or primary intracellular oxidation (Mouchet, 1992) of iron by *Gallionella* has not been proven, this hypothesis is supported by the fact that the iron bacterium has been developed in ferrous-containing mineral media and is sensitive to some organic matter, except at very low concentrations (Starkey, 1945; Wolfe, 1958).

The microorganisms of the *Sphaerotilus-Leptothrix* group, listed as heterotrophs or facultative autotrophs, are also thought to oxidize reduced forms of iron (Mulder and Deinema, 1981). However, the oxidation is not universally considered enzymatic because most of these iron bacteria develop in the pH range (6 - 8) in which autooxidation of iron occurs (Mulder and Deinema, 1981). It has been suggested that oxidation and accumulation of mineral iron by autotrophs in this group are achieved with extracellular polymers such as polysaccharides, proteins or polysaccharide-protein-lipid complexes (Rheinheimer, 1992). The genus *Gallionella* is also thought to demonstrate this mechanism, termed secondary extracellular oxidation by Mouchet (1992), where the extracellular material is produced in the form of the stalk which becomes encrusted with iron precipitates.

In the presence of iron-organic complexes, the heterotrophs in the *Sphaerotilus-Leptothrix* group and of the genera *Sidercapsa, Naumanniella, Ochrobium* and *Sidercoccus* are capable of obtaining the bound organic matter, thereby liberating the mineral iron to autooxidation (Ehrlich, 1990; Mouchet, 1992). As with the above case, the mineral iron is then accumulated through the use of extracellular polymers.

A fourth possible explanation for iron precipitation in the biological environment has been put forth to be metabolically-produced hydrogen peroxide (H_2O_2) which acts as a chemical oxidizing agent (Ehrlich, 1990). Two bacteria which have exhibited this mechanism in iron and/or manganese oxidation are: *Leptothrix pseudo-ochracea* and *Metallogenium* (Zavarin, 1981; Ehrlich, 1990).

For all bacterial uptake of iron, the precipitates are slightly hydrated iron oxides in the forms of lepidocrocite, γ-FeOOH, and goethite, α-FeOOH (Mouchet, 1992). These crystalline compounds are much more compact than the precipitates formed during chemical oxidation (ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$, and iron hydroxide, $Fe(OH)_3$), leading to the formation of a denser sludge in the biological process than in the physico-chemical process (Mouchet, 1992). In the transition between the biological and the physico-chemical environment, lepidocrocite is replaced by ferrihydrite (Vuorinen et al., 1988).

2.3.3 Growth conditions of iron bacteria

Numerous species of iron bacteria considered significant for drinking water treatment have been identified in their natural habitats. These include the following filamentous species: *Leptothrix lopholea, L. ochracea, L. pseudo-ochracea, L. discophora, L. cholodnii, Sphaerotilus natans, Crenothrix polyspora, Clonothrix fusca,* and *Lieskeella bifida* (Mulder and Deinema, 1981). *Leptothrix ochracea* and the sole stalked species thought to exist, *Gallionella ferruginea*, are considered the most prevalent iron bacteria (Hanert, 1981a; Starkey, 1945).

The natural habitat of *G. ferruginea* is very pure, iron-bearing water which contains only trace organics (Hanert, 1981a). From laboratory studies, a favourable

environment has a slightly acidic pH (6.0 - 7.6) and an oxidation-reduction potential between +200 and +320 mV (Wolfe, 1964; Hanert, 1981a). These conditions, when located on Figure 2, correspond with the zone of ferrous iron stability. Other parameters for cultivation of *G. ferruginea* are dissolved oxygen content between 0.1 and 1 mg/L, temperature between 8 and 16°C, ferrous iron content between 5 and 25 mg/L, dissolved carbon dioxide content ≥ 20 mg/L, and low organic matter content (Hanert, 1981a).

Similar to the *Gallionella* species, *Leptothrix ochracea* occurs in slowly running, iron-containing water which is poor in readily decomposable organic material (Mulder and Deinema, 1981). As previously mentioned, the favourable pH range is between 6 and 8 for accumulation of iron. *L. ochracea* has been found in temperatures ranging from 1 to 25°C, where the optimum is reported to be 15°C (Starkey, 1945).

The better known species of the Siderocapsaceae family include: *Sidercapsa treubii, S. major,* and *Naumanniella neustonica.* Several Siderocapsaceae species have been identified in deep wells and water pipes, such as *Sidercapsa botryoides, Naumanniella pygmaea, N. elliptica, N. minor, N. catenata, Siderobacter gracilis, S. brevis,* and *S. latus* (Hanert, 1981b). Favourable conditions reported for these organisms include low temperature (10 - 20°C), low dissolved oxygen concentration (0.1 - 1 mg/L) and the presence of organic matter (Starkey, 1945; Hanert, 1981b). Although no optimum pH level is given for the deep well species, an optimum range of neutral to pH 8.7 is reported for organisms in soil and lake habitats and an optimum range of pH 6 to 7 is reported for Siderocapsaceae species in swamps, ditches, and stagnant pools (Hanert, 1981b).

Two species of the genus *Metallogenium* have been identified: *M. personatum* and *M. symbioticum* (Zavarin, 1981). These are reportedly found in places containing manganese, including lakes, sediments, and soils (Zavarin, 1981). Typical parameters for development include a pH range from 4.1 to 8.9, Eh from +200 to +650 mV, manganese concentration $\leq$ 50 mg/L and oxygen concentration from 0.01 to 10 mg/L (Zavarin, 1981).

2.3.4 Full-scale application of biological iron removal

In current water treatment practice, bacterial germination on a sand filter is accomplished by artificial or natural means. Artificial germination introduces sludge from the backwash of an operating biological filter into the new filter. A natural germination is carried out by adjusting the chemical parameters of the raw water to suit the needs of the desired iron bacteria. If the raw water is suitable for biological iron removal, this practice should take between 2 to 5 days to complete.

Suitable raw water should contain no material which is considered to be toxic to the sensitive bacterial species (i.e., *Gallionella*). This can include hydrogen sulfide (H_2S), heavy metals or organic pollutants. Baas-Becking and colleagues have studied the area of iron bacteria activity in terms of aquatic pH and Eh conditions, as shown in Figure 9 (Wolfe, 1964; Mouchet, 1992). The lower limit in Figure 9 corresponds to rH = 14, where rH represents the negative logarithm of the hydrogen ion concentration producing the existing redox conditions (Rheinheimer, 1992). This can be expressed by the following equation:

$$rH = \frac{Eh}{c} + (2 \cdot pH) \qquad (10)$$

where Eh is expressed in millivolts (mV) and c is a constant equal to 0.029 mV^{-1} (Degrémont, 1991).

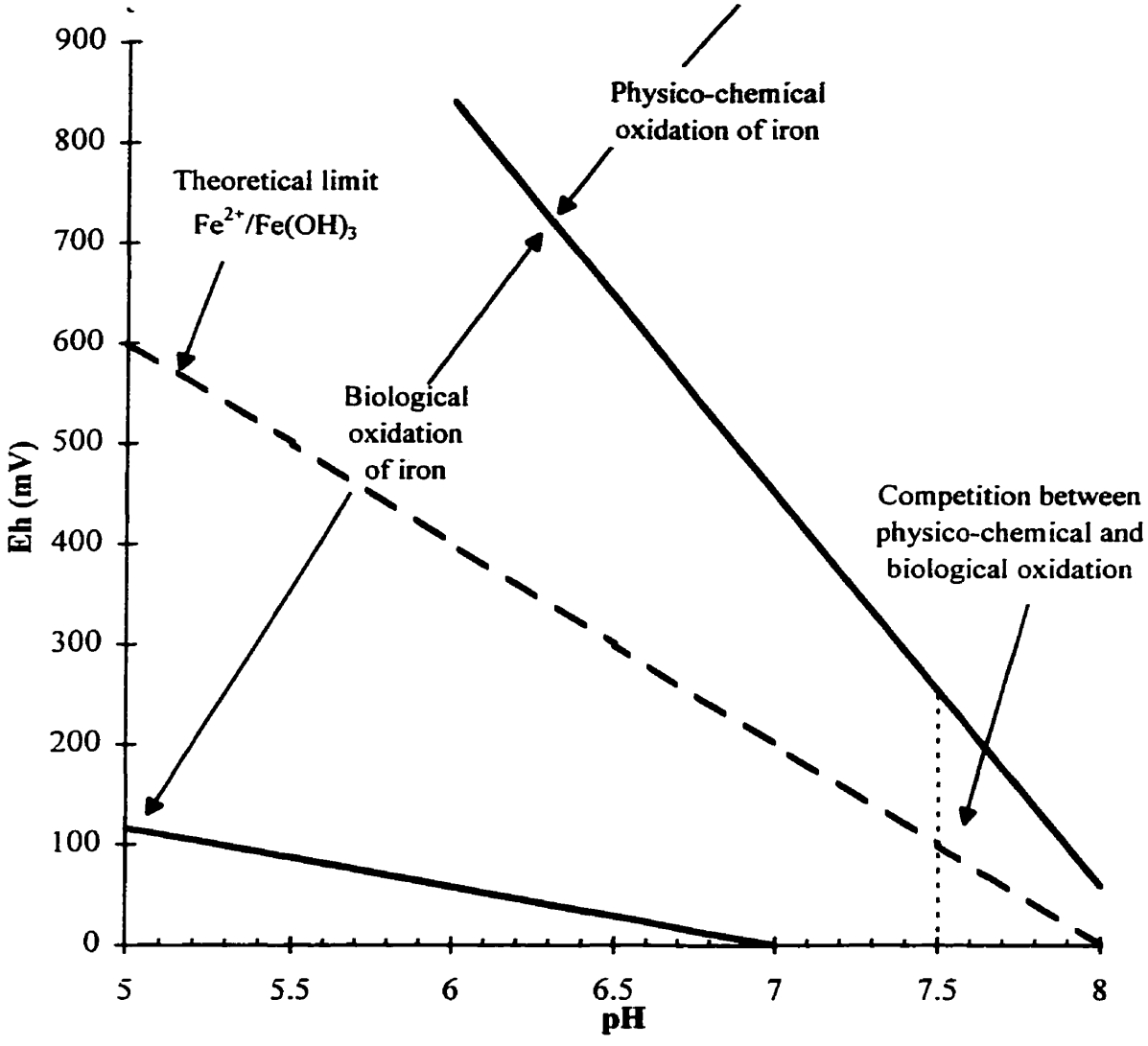

Figure 9. pH-Eh diagram of iron bacteria activity (after Mouchet, 1992).

The upper limit is also indicated but seems only to be of importance when the pH exceeds approximately 7.2, at which point biological action competes with physico-chemical oxidation (Mouchet, 1992). It should be noted that the biological region straddles the theoretical boundary between the region of ferrous ion stability and ferric hydroxide precipitation. This is related to the fact that iron bacteria which rely on iron oxidation as a source of energy are gradient organisms, meaning that they are not likely to develop under strongly reducing or strongly oxidizing conditions, but rather at the point where they have a source of both ferrous ions and air (Wolfe, 1964).

In general, a pH range from 6 to 8 is recommended and the corresponding Eh range can be determined from Figure 9. Dissolved oxygen is a variable which is adjusted per installation, according to the pH (increasing dissolved oxygen increases Eh) and the needs of the aerobic or microaerophilic bacteria (Mouchet, 1992).

When the raw water is suitable for the development of iron bacteria, biological elimination of iron is the method of choice over physico-chemical treatment for several reasons. Chemical oxidants, coagulants, and flocculants are not required and aeration can be achieved with in-line air injection (Degrémont, 1991). A higher flow rate is possible (20-40 m/h superficial velocity), meaning more throughput can be achieved (Degrémont, 1991). Because of the bacterial action in accumulating the iron oxides, sand with a larger effective size (1.18 to 2.05 mm) can be employed (Mouchet, 1992), which facilitates the higher-flow operation. Also, the overall space requirements for the plant are reduced since oxidation and filtration stages are combined into a single reactor (Mouchet, 1992). And finally, a higher removal capacity is realized, generally on the order of 2 to 5 kg per m^2 of filter cross sectional area, (Mouchet, 1992).

As with conventional processes, filtered water is disinfected (usually with chlorine) before discharge to the water distribution network and a backwash using raw water and air scour is required periodically to regenerate the filter.

2.4 Oxidation-Reduction Potential

The concept of oxidation-reduction potential (ORP) comes from the exchange of electrons among chemical species in a given medium. These species can exist in either reduced or oxidized form and are transformed from one to the other by either the acquisition of electrons (reduction) or the loss of electrons (oxidation) in what are called redox (oxidation-reduction) reactions. These reactions depend upon chemical conditions of the system and the bacteria which mediate redox reactions.

Redox reactions occur in pairs such that the species being oxidized is the reducing agent and the species being reduced is the oxidizing agent. For example, the redox reactions for the oxidation of iron and the reduction of oxygen are expressed as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{11}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{12}$$

Adding the above equations, balancing and canceling the electrons gives the following reaction, a slightly modified version of reaction (1).

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^{-} \tag{13}$$

The capacity of a system to donate or receive electrons is expressed with ORP, which is determined by the Nernst equation (Charpentier et al., 1987):

$$E_o = E_o^0 + \frac{RT}{nF} \log \frac{[ox.]}{[red.]} \tag{14}$$

E_o = redox potential measured by the electrode

E_o^0 = standard potential of the system at equilibrium

R = ideal gas constant (8.314 J/K/mole)

T = absolute temperature (K)

n = number of electrons

F = Faraday's constant (96 500 coulombs/mole)

$[ox.]$ = concentration of oxidized matter (mg/L)

$[red.]$ = concentration of reduced matter (mg/L)

The measurement of redox potential requires a standard reference which is, by convention, the universal hydrogen electrode. Because the hydrogen electrode is not practical to use in most applications, another reference is used as the internal electrode reference to the measuring electrode. However, the redox potential is always expressed in terms of the universal reference, according to the following expression:

$$E_H = E_a + E_{ref} \qquad (15)$$

E_H = potential in terms of the universal hydrogen electrode

E_a = potential in terms of the internal electrode (measured)

E_{ref} = standard potential of the internal electrode

In biological wastewater treatment, the ORP-time profile has been correlated with biological activity related to redox reactions (Wareham et al., 1993). The relationship of ORP to dissolved oxygen (DO) has also been investigated as a way to optimize aeration of activated sludge reactors and energy savings (Charpentier et al., 1987; Heduit and

Thevenot, 1989). ORP has the advantage over the traditional dissolved oxygen indicator in that ORP is still significant when DO levels approach zero (Charpentier et al., 1987).

Clearly, the above features of using ORP to monitor a water treatment system may be applied in drinking water treatment. Also, ORP in conjunction with pH is crucial in determining whether or not the requirements for bacterial development are met, and if physico-chemical oxidation of iron will compete with bacterial oxidation, as indicated in Figure 9. Thus, the application of ORP as a control tool in drinking water treatment systems represents a promising area of study.

3. METHODS AND MATERIALS

3.1 PRESENTATION OF THE SITES

Two similar sites of full-scale scale drinking water treatment facilities were selected for the study. Both plants are equipped with two biological filters which operate in series to carry out biological iron and manganese removal. The study was organized into several phases at each site, as depicted in the following table. Each site and its facilities will be described initially, followed by a discussion of the materials installed at each site and methods used.

Table 2. Organization of the study at two sites.

I. Seignosse		**II. Septmonts**	
Phase	**Date**	**Phase**	**Date**
A. Primary filter	June - July 1996	A. Biological pilot	November 1996
B. Biological pilot	Aug. - Oct. 1996	B. Catalytic pilots	December 1996
C. Primary filter	October 1996	--	--

3.1.1 Seignosse

Seignosse is a seaside town in the southwest corner of the France where the plant operates during the summer months on an intermittent basis, producing drinking water at a rate of about 1000 m^3 per day. The primary filter bed measures 1 m in depth, has a cross sectional area of 3.14 m^2 and consists of sand with an effective size of 1.18 mm. In total, the reactor stands 3 m in height. The second filter has similar dimensions to the

primary filter with the exception of a slightly larger cross sectional area which measures 4.52 m^2. Figure 10 shows a schematic of the full-scale plant.

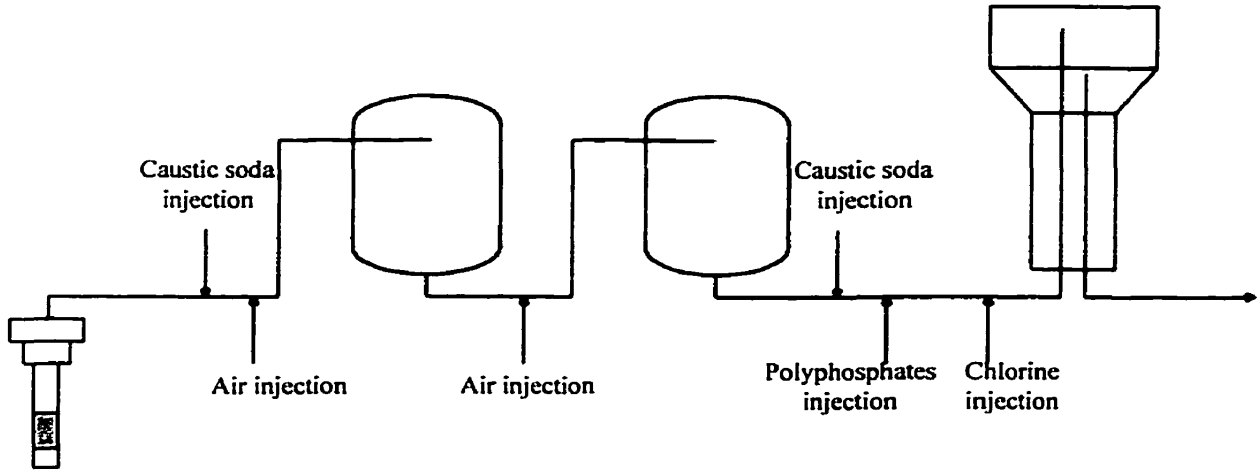

Figure 10. Drinking water treatment facilities in Seignosse.

The raw water was analyzed in June and July to give the average parameters and standard deviations which are summarized in Table 3. A complete set of biological and chemical analyses were carried out on a regular basis by the local laboratory. A copy of analyses performed in July 1996 on the raw water is contained in Appendix 1.

Before entering the primary filter, as shown in Figure 10, the raw water was injected with caustic soda solution and air to increase pH to within the neutral range and to increase the DO content. The superficial velocity of filtration was approximately 30 m/h which corresponded to a flowrate of 70 m^3/h. Average pressure drop across the filter during a filtration cycle was approximately 20 kPa. Gauge pressure measured at the head of the filter varied between 470 and 500 kPa during the filtration cycle. A backwash of

the primary filter using raw water and air scour was carried out after every 500 m^3 (approximately 7 hours) of filtration.

Table 3. Seignosse mean raw water parameters ± standard deviation, June 1996.

Total iron (mg/L)	3.80 ± 0.19
Dissolved iron (mg/L)	3.61 ± 0.14
Total manganese (mg/L)	0.042 ± 0.002
Dissolved manganese (mg/L)	0.042 ± 0.001
pH	5.73 ± 0.03
Eh (mV)	288 ± 7
Dissolved oxygen (mg/L)	0.00 ± 0.00

Air was injected a second time to the primary filtered water before it was delivered to the second filter. Pressure fluctuation during a cycle of the second filter was similar to the first, though it filtered 2 500 m^3 per cycle. Thus a backwash of the second filter using raw water and air scour was carried out with every fifth regeneration of the primary filter.

At the exit of the second filter, caustic soda was injected a second time, the water was chlorinated and polyphosphates were added to inhibit corrosion. Finally, the treated water was sent to the water tower (chateau d'eau) for distribution.

3.1.2 Septmonts

The water treatment plant in Septmonts functions on an intermittent basis (10 - 13 hours per day) nearly year round to produce drinking water for the local community. The treatment plant in Septmonts also consists of two biological filters in series.

Schematically the plant is similar to the facilities in Seignosse as represented in Figure 10. The research at this site was concerned essentially with studying biological and catalytic treatment of the raw water on pilot scale. Therefore, further details of the plant itself are not presented. Raw water parameters are compiled in Table 4. The raw water also contained 0.4 mg/L of ammonium and a low concentration of hydrogen sulfide (0.01 mg/L).

Table 4. Septmonts mean raw water parameters ± standard deviation, November 1996.

Total iron (mg/L)	3.82 ± 0.82
Dissolved iron (mg/L)	3.47 ± 0.74
Total manganese (mg/L)	0.317 ± 0.019
pH	6.70 ± 0.06
Eh (mV)	174 ± 27
Dissolved oxygen (mg/L)	0.16 ± 0.11

3.2 MATERIALS

3.2.1 Installation on site at Seignosse

In order to enable sampling of filtered water and measurement of chemical parameters, a valve at the exit (base) of the primary filter was tapped and used to continually supply a 22 L open air tank which overflowed to the drain. An automatic valve was used to halt flow to the tank whenever the plant was not in operation.

The tank also served as a probe bath to measure parameters such as pH, Eh, and DO. Polymetron pH and Eh probes were furnished by Zellweger Analytical. The ORP

probe had a platinum ring electrode and contained an internal reference solution of Ag/AgCl. The internal reference potential (E_{ref}) of 198 mV was used to calculate the standard potential measurements. The oxygen probe utilized was the Oxi 323-B by WTW (Germany). Electrochemical measurements were related to a data acquisition system through a central processor equipped with a 10 channel input/output (I/O) multiplexer card.

3.2.2 Biological pilot plant at Seignosse

Figure 11 shows the schematic of the pilot constructed in August 1996. Sand of 1.35 mm effective size filled the polyethylene column to a 1 m depth. In total, the pilot measured 3 m in height, with an inside bed cross sectional area of 0.005 m^2. All valves and nozzles were of PVC construction.

A sampling port on the raw water inlet line to the plant was tapped to supply the pilot. An automatic valve was used to halt flow to and from the pilot when the plant was not in operation. Compressed air from the plant was used for in-line air injection to the pilot. Air and water flow for both normal operation and backwashing were controlled using rotameters.

A 22 L open air tank was placed at the exit of the pilot to facilitate sampling and measurement of pH, Eh, and DO concentration. Continuous measurement of electrochemical parameters was achieved with the same equipment described in the last section.

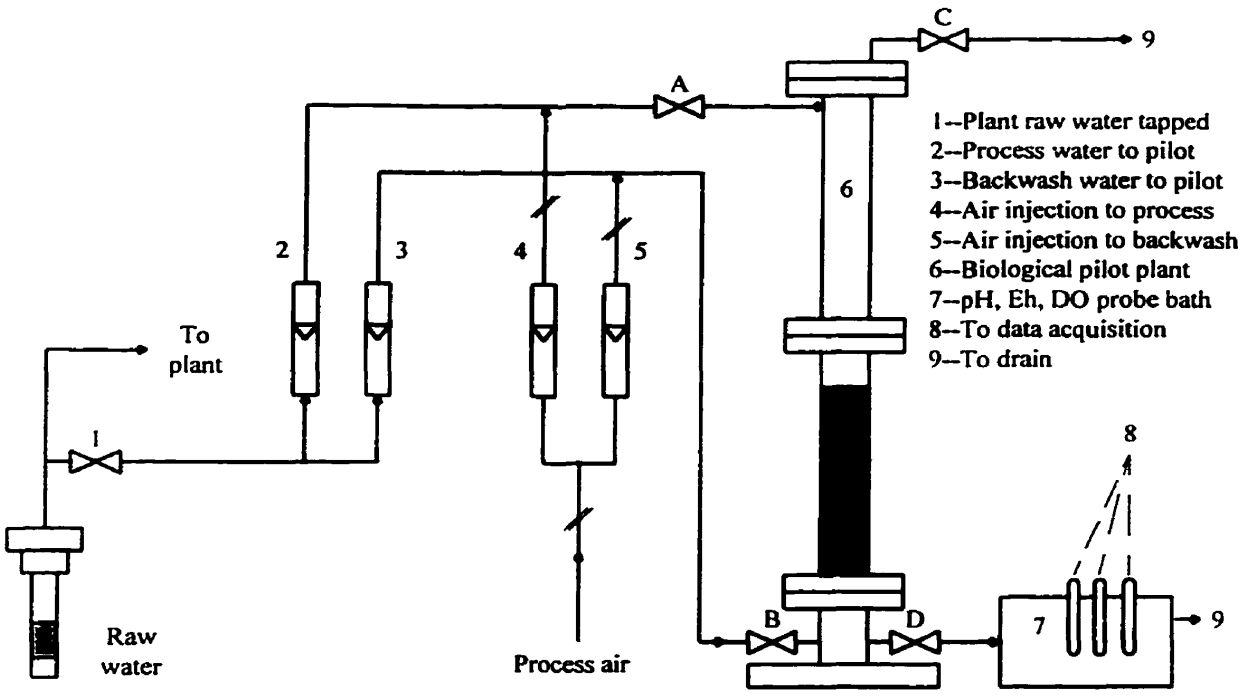

Figure 11. Biological pilot plant facilities in Seignosse.

Initial gauge pressure at the head of the filter was regulated to 50 kPa using the valve on the exit line of the filter. Pressure drop across the filter was calculated as the difference in water level between the inlet of the column and the outlet (open air tank). A difference in height of approximately 2.3 m gave an initial pressure drop of 23 kPa. Superficial velocity was established at 45 m/h (225 L/h) and air injection equivalent to 0.6 mg/L DO in the filtered water. Raw water and air scour were used to perform a backwash (valves A and D closed; valves B and C open) when the gauge pressure increased above approximately 100 kPa or filter saturation was perceived.

3.2.3 Biological pilot plant at Septmonts

An identical biological pilot plant to the one in Seignosse was constructed in Septmonts at the end of October 1996. However, the raw water was supplied by a separate pump which was lowered 14 m (dynamic hydraulic level) into the well where the raw water for the full-scale operation was being drawn. Compressed air was obtained from the plant and was controlled using a separate rotameter. The same materials were used as in the last two sections to continually measure pH, Eh, and DO concentration.

Initial gauge pressure was regulated to 50 kPa, resulting in a pressure drop of approximately 26 kPa. Superficial velocity was set to 14 m/h (70 L/h) and air injection equivalent to approximately 1.00 mg/L DO in the filtered water. Raw water flow to the pilot was controlled by adjusting the variable frequency on the pump. Raw water and air scour were used to regenerate the filter when the gauge pressure increased above approximately 100 kPa or filter saturation was detected.

3.2.4 Catalytic pilot plants at Septmonts

After having completed the study of biological treatment of iron on pilot scale, the pilot was dismantled, the sand removed and the interior rinsed. The polyethylene column was then charged with *Ferrolite MC2* to a 1.2 m depth. A second identical polyethylene column was assembled and filled with *Purolite* to a 1.2 m depth. Both products were black granular material having smaller effective sizes than the sand used previously in the biological filter. Thill (1995) determined the effective size to be 0.52 mm and 0.27 mm and the bulk density to be 1120 kg/m^3 and 1370 kg/m^3 for *Ferrolite MC2* and *Purolite*, respectively.

It was not possible for the two columns to operate simultaneously under pressure as in the case of the biological pilots. However, it was desirable to be able to inject air to the raw water, and since the columns were open to the air at the top, it was necessary to reverse the flow with respect the previous pilot studies. Thus filtration took place with raw water entering at the base of the column and flowing out through a valve near the top. A schematic of the two catalytic pilots is shown in Figure 12.

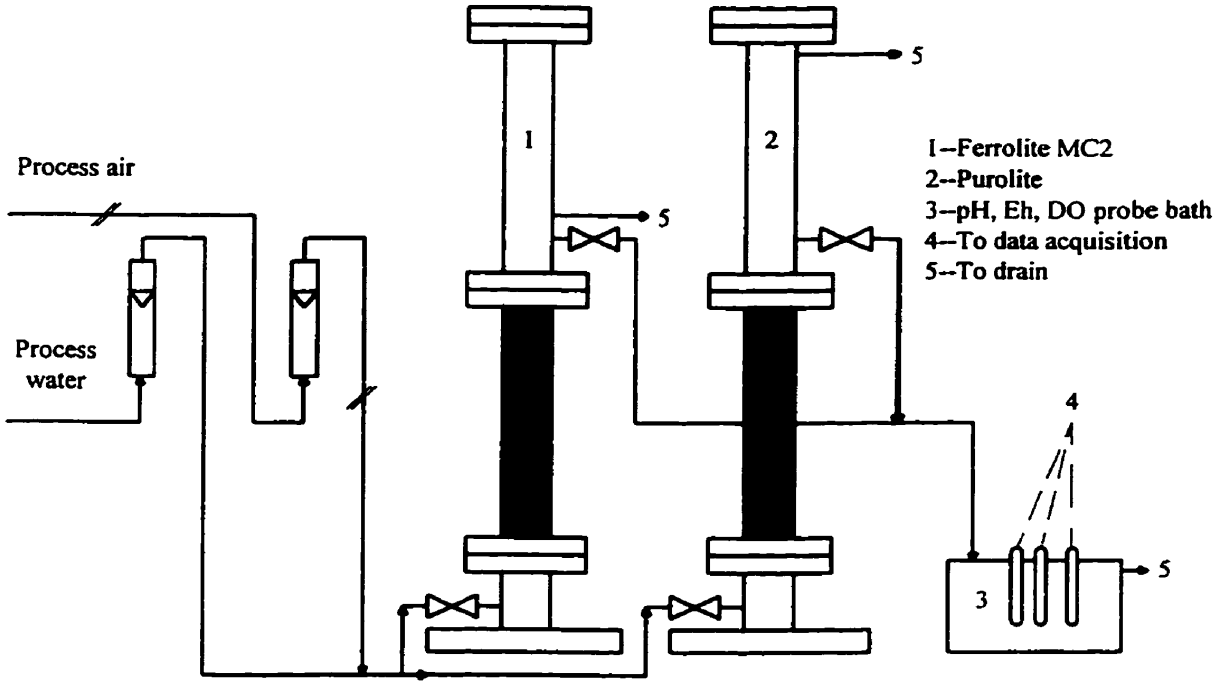

Figure 12. Catalytic pilot plant facilities in Septmonts.

Flow to both columns was modified using the adjustable frequency on the pump and total flow was indicated by a single rotameter, as was the air injection to the raw water. If both pilots were operating simultaneously, the flowrate at the exit of one

column would be measured with a graduated cylinder. Often one column or the other would operate alone, since only one set of measuring probes were available during experimentation. The hydraulic depth of each filter bed was 1.08 m and 1.12 m for the *Purolite* and *Ferrolite MC2*, respectively.

3.3 Analytical Methods

Throughout the various phases at each site, analytical methods and maintenance protocol were consistent.

3.3.1 Electrochemical measurements

The pH probe was calibrated frequently using buffer solutions of pH 4.01 and pH 7.00. The DO probe was equipped with its own calibration capsule which simulated an atmosphere of air saturated with water. A comparison of the DO reading with literature values for air at 100% relative humidity and the given temperature were then used to determine the accuracy of the reading. If the DO measurement was not within ± 0.01 mg/L of the standard references, the probe required membrane or electrolyte replacement.

The ORP probe was verified periodically with 230 mV buffer solution and the platinum ring was polished daily during the trials. Instrument literature indicated a measuring precision of ± 10 mV.

3.3.2 Sampling

Collection of water samples for chemical analysis was achieved with wide-mouthed plastic bottles. All samples for chemical analysis had to be obtained quickly, but without agitation (no mixing with air), and immediately analyzed to ensure sample integrity. This

was especially true of raw water samples which were effectively free of oxygen. Thus, upon mixing with air, there was a possibility of altering the iron (manganese) species due to dissolution of oxygen and evacuation of carbon dioxide.

For the full-scale plant at Seignosse, raw water was collected from a valve on the inlet to the primary filter (before caustic and air addition). Similarly on the pilot plants, raw water samples were taken from a valve on the inlet to the pilot before air injection. The valve was connected to a hose or tubing which was placed at the bottom of the sampling bottle. Sampling was complete once the volume was overturned several times.

Filtered water samples were collected from the open-air tank. The sampling bottle was first rinsed then filled with the desired sample.

Samples of raw water after the addition of caustic and air were taken from the full-scale facilities at Seignosse in a similar fashion to collection of raw water samples. Aerated raw water samples were also taken from the biological pilots through sampling ports located above the filter bed of the column.

During the study of the full-scale facilities in Seignosse, some samples of secondary filtered water were also analyzed. These were taken from the laboratory sink faucet during off-season (June and October 1996), as it was directly supplied with water from the second filter. From July to September, the tap water was chlorinated which would have affected composition, thus secondary filtered water was obtained from an upstream sampling port.

3.3.3 Chemical analyses

Analysis of total and dissolved iron and manganese were performed with the DR2000 spectrophotometer from HACH. All methods used were documented in the accompanying instrument manual (HACH, 1992). All reagents were furnished by HACH. The differentiation between total and dissolved species was achieved by filtering samples on individual disposable 0.45 μm membranes by Millipore. Samples with concentrations exceeding the upper concentration limit for the iron determination method were diluted 1:10 with demineralized water.

The HACH method 260 for analysis of iron gave readings with precision of ± 0.0027 mg/L and the method 290 for analysis of manganese indicated values with precision of ± 0.0049 mg/L.

3.4 Experimental Methods

3.4.1 Normal operation of the facilities in Seignosse

The first sets of experiments were carried out between late May and early June on the full-scale scale facilities in Seignosse. During this time, it was possible to manipulate the start-up of plant operation in order to evaluate the effect of long periods of downtime on the concentration of iron in the raw water. The evolution of residual iron in the filtered water after the backwash was also studied to determine "maturation time" or time until the lowest residual iron concentration was achieved in the filtered water.

For the first of these objectives, the full-scale plant was stopped overnight then put back into operation in the morning. During the ensuing cycle, both the raw water and

filtered water were analyzed periodically for concentrations of total and dissolved residual iron, and occasionally for manganese. Corresponding electrochemical measurements (pH, Eh and DO concentration) were also recorded.

To evaluate the maturation time, an automatic timer was used to start the plant up during the night. Thus a backwash was effectuated automatically during the day and the evolution of total and dissolved residual iron over the length of the following cycle was monitored while the corresponding electrochemical measurements of pH, Eh and DO concentration were noted.

A second set of experiments, also concerning normal operation of the full-scale facilities, were carried out in July. At this time the plant was operating intermittently, based on a signal indicating the level in the reservoir. During this peak period, the plant was found to be operating up to 14 hours over a 24 hour period or two hours at a time with approximately one hour of downtime between times of operation. Residual iron concentration and electrochemical measurements were recorded during times of operation.

3.4.2 Aeration-ORP trials

The aeration-ORP trials involved several aims, the first of which was to establish the influence of dissolved oxygen on biological treatment of iron. Secondly, the relationships between ORP and both DO concentration and residual iron concentration in the filtered water were investigated. Lastly, ORP was evaluated as an indicator of biological iron removal from drinking water.

Over the course of several days, air injection to the raw water was varied. After each modification, the pH, Eh, DO concentration, total residual iron and dissolved residual iron of the filtered water were systematically recorded.

These trials were carried out on the primary filter of the full-scale facilities at Seignosse in June. The air injection was adjusted one hour after the backwash had been completed. Sampling and analysis were then performed every fifteen minutes for the first two hours and every hour following up until 3 hours into the next cycle (approximate length of one cycle was 7 hours). During each run, periodic samples of raw water were also collected and analyzed for iron.

Aeration-ORP trials were performed on the biological pilots in Seignosse (October 1996) and Septmonts (November 1996). Because the pilots tended to operate for longer periods of time, sampling and recording of electrochemical measurements with each adjustment of air were only performed until parameters and residual iron were stable.

3.4.3 Catalytic trials

Initial operation of the catalytic pilot columns was aimed to remove the fine particulate matter of the filter bed, or "fines". This process was quite lengthy because of the reverse flow configuration, and some fines still escaped with the exiting filtered water during experimentation. Thus nearly all samples analyzed for iron and manganese were first filtered to focus on evaluating the oxidation capacity of the catalytic materials. Each material was tested at different velocities and various levels of DO concentration in the filtered water.

4. RESULTS AND DISCUSSION FOR SEIGNOSSE

4.1 Initial Study on Full Scale

4.1.1 Normal operation

Raw water iron content and composition may be affected by long periods of downtime. One contributing factor is a low groundwater velocity which increases the contact time between the water and minerals containing iron. Also, when the pump is in operation, the water table descends, forming a vortex around the pump. The wetted minerals above the vortex are exposed to air, resulting in the formation of precipitates. When pumping stops, the water level returns to normal and precipitates are re-entrained in the groundwater. These precipitates are taken up by the pump once operation resumes. Thus overnight stoppage is studied to evaluate the impact of these factors on the iron removal process.

After startup of the pump, a certain period of time is needed for the raw water quality to become more or less stable. This is observed in Figure 13, showing the evolution of raw water quality over a six hour period on two separate days after startup. The mean values for the entire cycle of each run in Figure 13 are summarized in Table 5 with their standard deviations. The mean values are also indicated for each run not including the first 100 minutes, where the iron content appears to be the most variable.

Table 5. Raw water quality evolution after startup.

Date	Total iron content (mg/L)	
	Entire cycle	Cycle less first 100 minutes
29/05/96	3.58 ± 0.16	3.50 ± 0.03
04/06/96	3.50 ± 0.09	3.52 ± 0.05

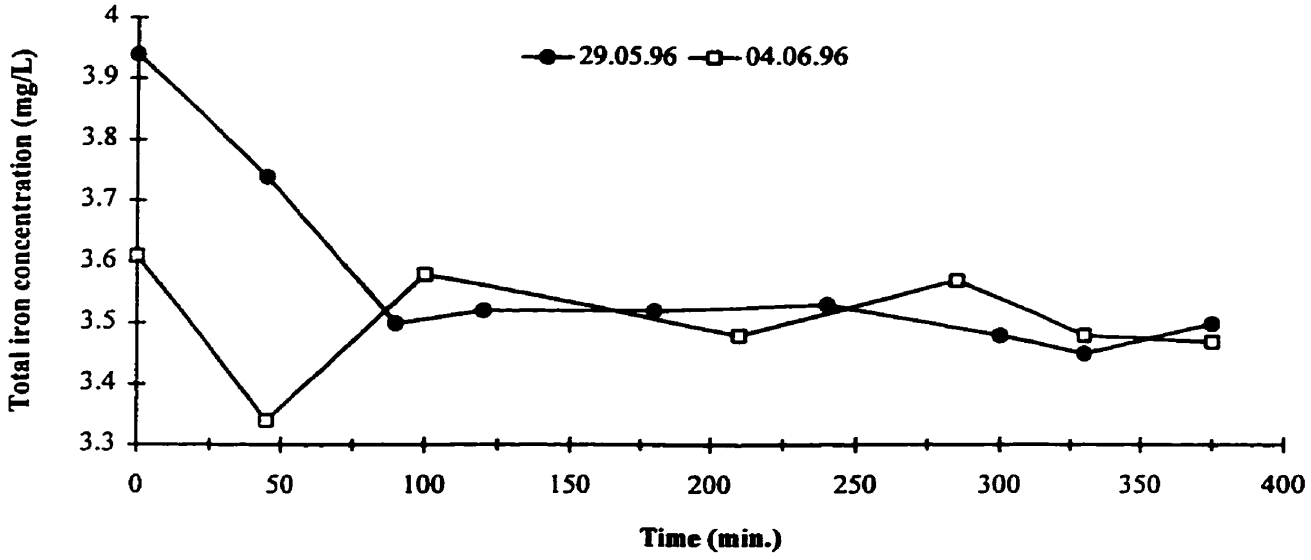

Figure 13. Evolution of raw water quality with plant startup after 14 hour downtime.

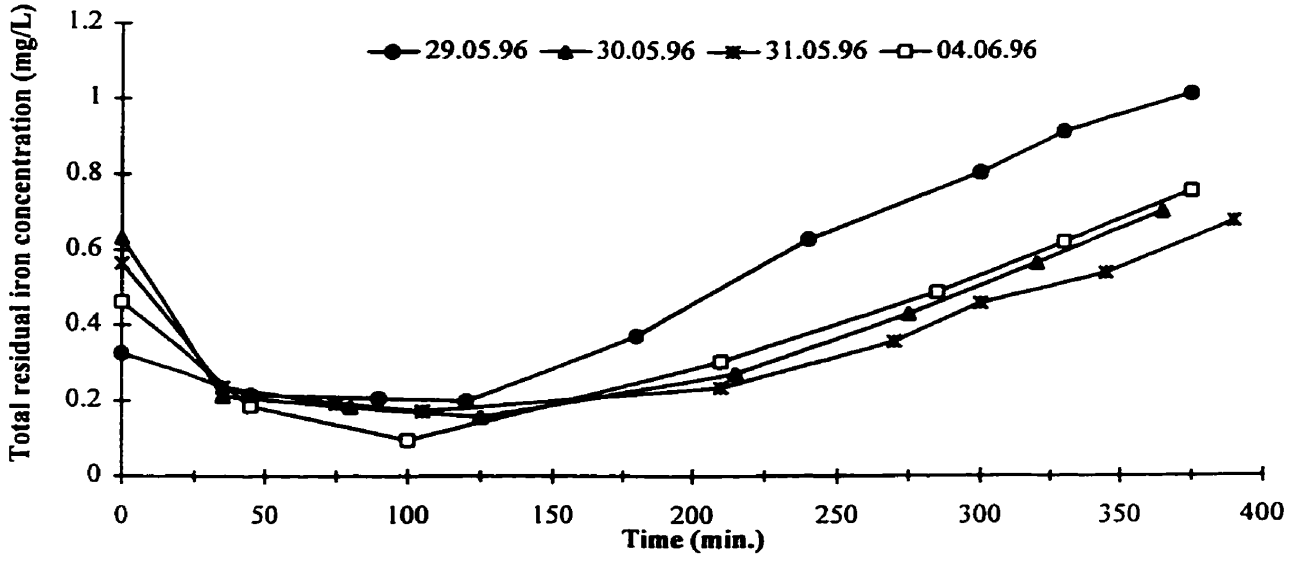

Figure 14. Evolution of residual iron after overnight stoppage and during filter maturation.

The results from the filter maturation study are illustrated by the evolution of total residual iron (TRI) in the filtered water over the length of two filtration cycles (7 hours) on two different dates (30/05/96 and 31/05/96), shown in Figure 14. The evolution of TRI on 29/05/96 and 04/06/96 corresponding to the raw water analyses from Figure 13 (after overnight stoppage) are also shown on the same plot. Figure 14 shows that the evolution of TRI appears to occur overall in the same manner; that is, after an initial decrease, TRI increases steadily towards the end of the cycle for the four sets of data. This observation was later thought to be attributed to physico-chemical oxidation which was taking place in the primary filter. This is further discussed in the next section.

The maturation time is determined as the time required for TRI to attain a minimum value. From Figure 14 the average maturation time was about 100 minutes.

It should be noted that for the filter maturation study, the total iron in the raw water was found to be much more variable on 30/05/96 (total iron = 3.74 ± 0.19 mg/L) than on 31/05/96 (total iron = 3.65 ± 0.06 mg/L). Despite the greater variation in raw water quality on 30/05/96, the evolution of filtered water quality was essentially the same for both cycles. Thus it seems that the treatment of iron was not affected by the observed variations in raw water iron content.

Normal operation of the full-scale facilities was also studied in July to evaluate the effect of intermittent operation on iron removal. The primary filter was in operation 14 hours per 24 hour period with a low air injection (DO = 0.2 mg/L). After each brief downtime, it was noticed that treatment appeared to recover immediately and filter maturation required approximately 30 minutes. This is illustrated in Table 6.

Table 6. Primary filter intermittent operation, July 1996.

Time (minutes)	Residual iron concentration upon startup (mg/L)	
	After intermittent interruption	After backwash
0	0.182	1.385
30	0.220	0.276
60	0.217	0.247
90	0.223	0.234
120	--	0.235

4.1.2 Aeration-ORP trials

The aeration-ORP trials on the primary filter evaluated dissolved oxygen levels varying between approximately 0 and 7 mg/L.

Figure 15 shows the evolution of Eh and DO concentration for the trials carried out on the primary filter in June. With each modification of air injection, the ORP measurement seemed to suggest a proportional relationship throughout the cycle with the DO concentration in the filtered water.

Figure 16 presents the changes in total and dissolved residual iron concentrations during the aeration-ORP trials, where the runs shown correspond to the runs indicated in Figure 15. By comparing the corresponding runs on Figure 15 and 16, it is observed that as DO increased in runs 1 through 5, the dissolved residual iron (DRI) content in the filtered water decreased nearly to zero.

A comparison of the two plots also shows that the TRI attained a maximum value at the end of the first filtration cycle in each run (recall that each trial consisted of monitoring conditions from the point at which the air injection was modified to the end of

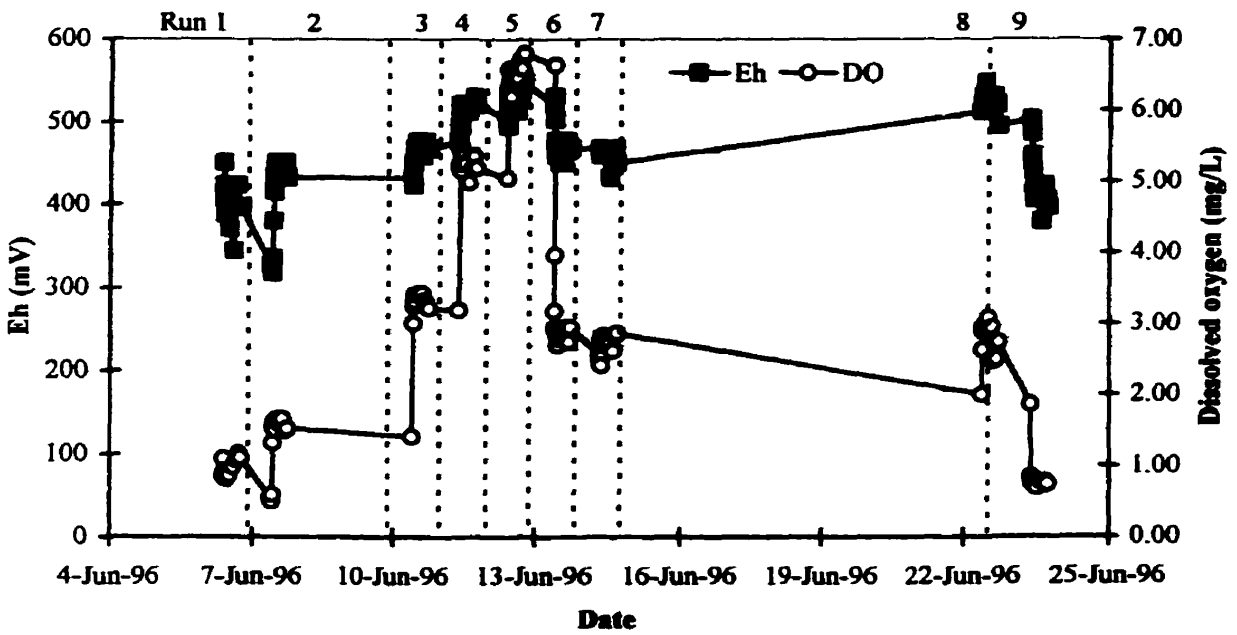

Figure 15. Evolution of DO and ORP during the aeration-ORP trials on the primary filter in June 1996.

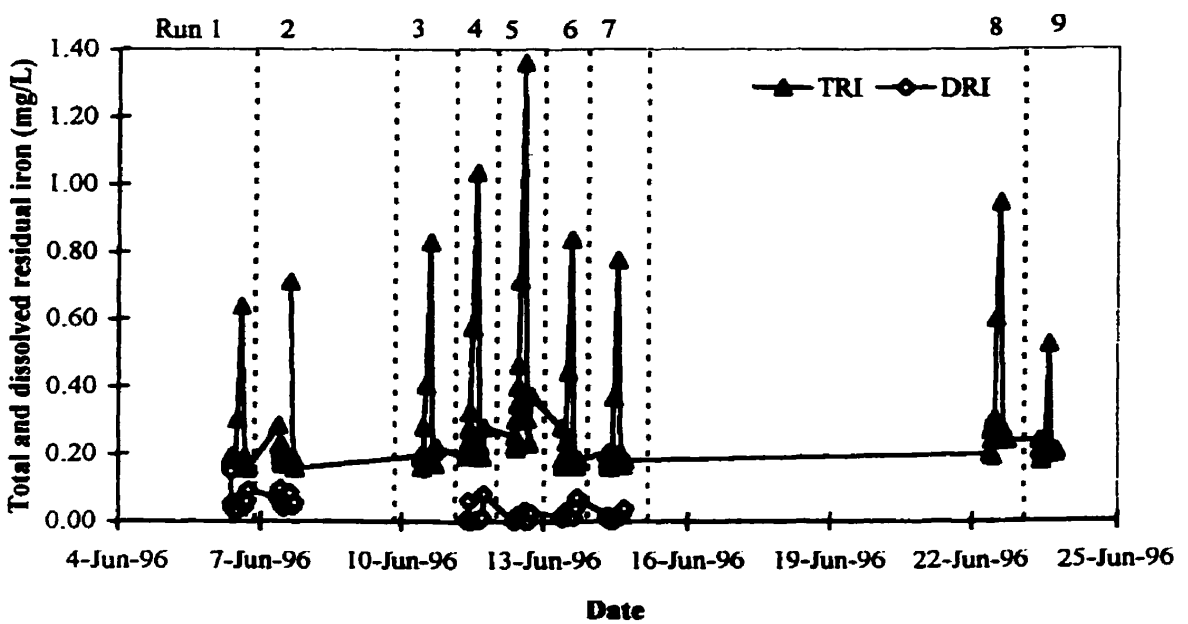

Figure 16. Evolution of total and dissolved residual iron during the aeration-ORP trials.

that cycle and up to 3 hours into the following cycle; or a total of approximately 9 hours of analyses). These results correspond to previous observations of an increase in TRI towards the end of the filtration cycle (Figure 14). The level of this maximum TRI attained seems to be proportional to DO levels in each run. Thus, it appears that increasingly poor retention was occurring as DO injection was increased.

It is postulated that filter operation was relying on a combination of physico-chemical and biological oxidation. Thus increasing the DO injection increased the proportion of physico-chemical oxidation taking place. And since the sand size in the filter (ES 1.18 mm) was suited to biological as opposed to physical retention, poor retention of precipitates was the observed result.

It was possible to establish a relationship between DO and Eh, as shown on Figure 17. A natural logarithm correlation was determined using Excel 5.0 software and rendered the following relationship, with a correlation coefficient (R^2) of 0.706.

$$Eh = 59.7 \cdot \log_e[DO] + 414.7 \qquad (16)$$

It is notable that the above relationship resembles the form of the correlation established between DO and Eh by Heduit and Thevenot (1989) in activated sludge reactors. Heduit and Thevenot (1989) found a slope between 55 and 65 mV and an intercept of 410 mV for sludge aerated for several hours without feeding (pH between 7 and 7.6).

The evolution of DRI with increasing DO is also shown in Figure 17. It appears that DRI tends to decrease with increasing DO, an observation which supports the earlier postulation of physico-chemical oxidation. It should be noted that linear correlations were investigated between DRI and DO as well as between TRI and DO but gave poor R^2 values, due to the spread in data throughout the filtration cycle.

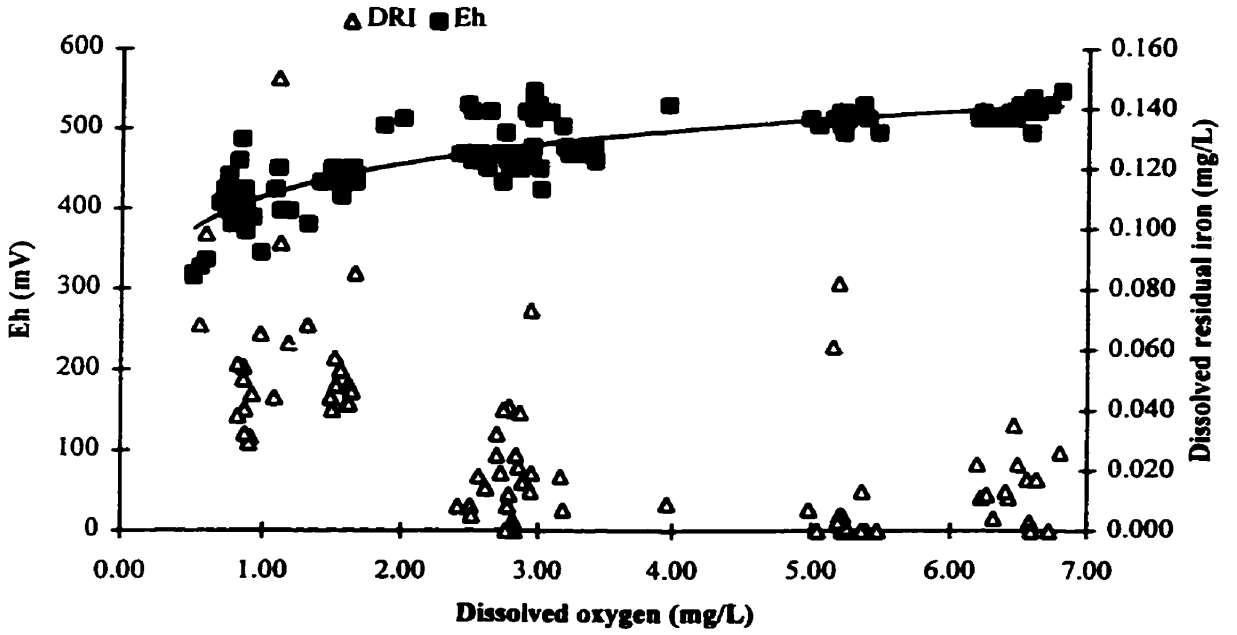

Figure 17. Relationship between DO and both ORP and DRI during the aeration-ORP trials

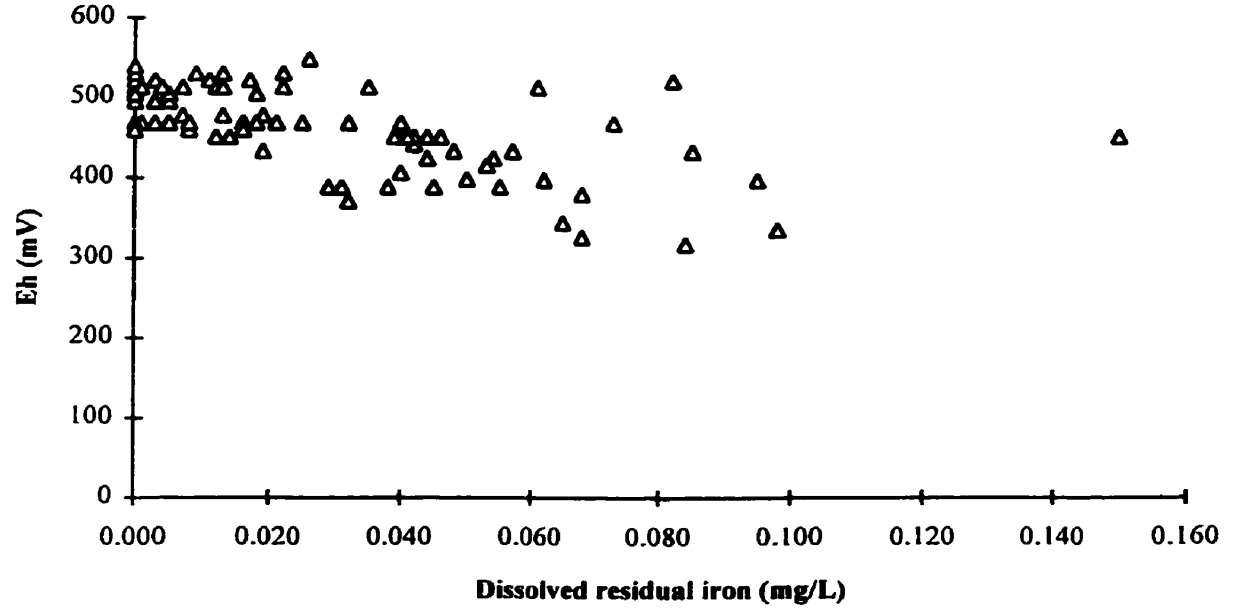

Figure 18. Relationship between ORP and DRI during the aeration-ORP trials.

Finally, a plot of Eh against DRI is presented in Figure 18, where it is suggested the ORP measurement decreases with increasing DRI. It should be noted that a linear correlation between Eh and DRI yielded a poor correlation coefficient (R^2) of 0.365. A similar relationship investigated between Eh and TRI yielded no identifiable trends.

Generally, the aeration-ORP trials revealed that the pH, Eh, DO, TRI and DRI rapidly achieved stable values after modification of the air injection. Overall, the plant was producing water which conformed to French regulation but the trials suggested that physico-chemical oxidation was a major factor in iron removal. Also, analyses of the backwash sludge did not reveal the expected iron bacteria (i.e., *Gallionella* or *Leptothrix*).

Further analyses were carried out in July on the raw water after the addition of caustic and air before it entered the primary filter (pre-filtered primary water). These analyses are summarized in Table 7 along with mean values for raw and primary filtered water. The results support the presumption of physico-chemical oxidation by indicating that 95 - 100% of total iron was in dissolved form in the raw water and only 25 - 28% was dissolved after the addition of caustic and air (before filtration).

Table 7. Water quality before and after primary filter, June and July 1996.

Water quality parameters	Mean values ± Std. Dev.		
	Raw	Pre-filtered primary	Primary filtered
Total iron (mg/L)	3.80 ± 0.19	4.82 ± 0.38	0.339 ± 0.277
Dissolved iron (mg/L)	3.26 ± 0.14	1.26 ± 0.04	0.130 ± 0.078
pH	5.73 ± 0.03	7.30 ± 0.12	6.91 ± 0.06
Eh (mV)	288 ± 7	157 ± 23	349 ± 60
Dissolved oxygen (mg/L)	0.00 ± 0.00	1.06 ± 0.09	0.40 ± 0.84

The above conditions of pH and Eh are placed on the pH-Eh diagram showing iron bacteria activity (Figure 9) and presented in Figure 19 to demonstrate that the raw water parameters were clearly in the region of iron bacteria activity. Points A, B, and C correspond to the raw water, the pre-filtered primary water and the primary filtered water, respectively.

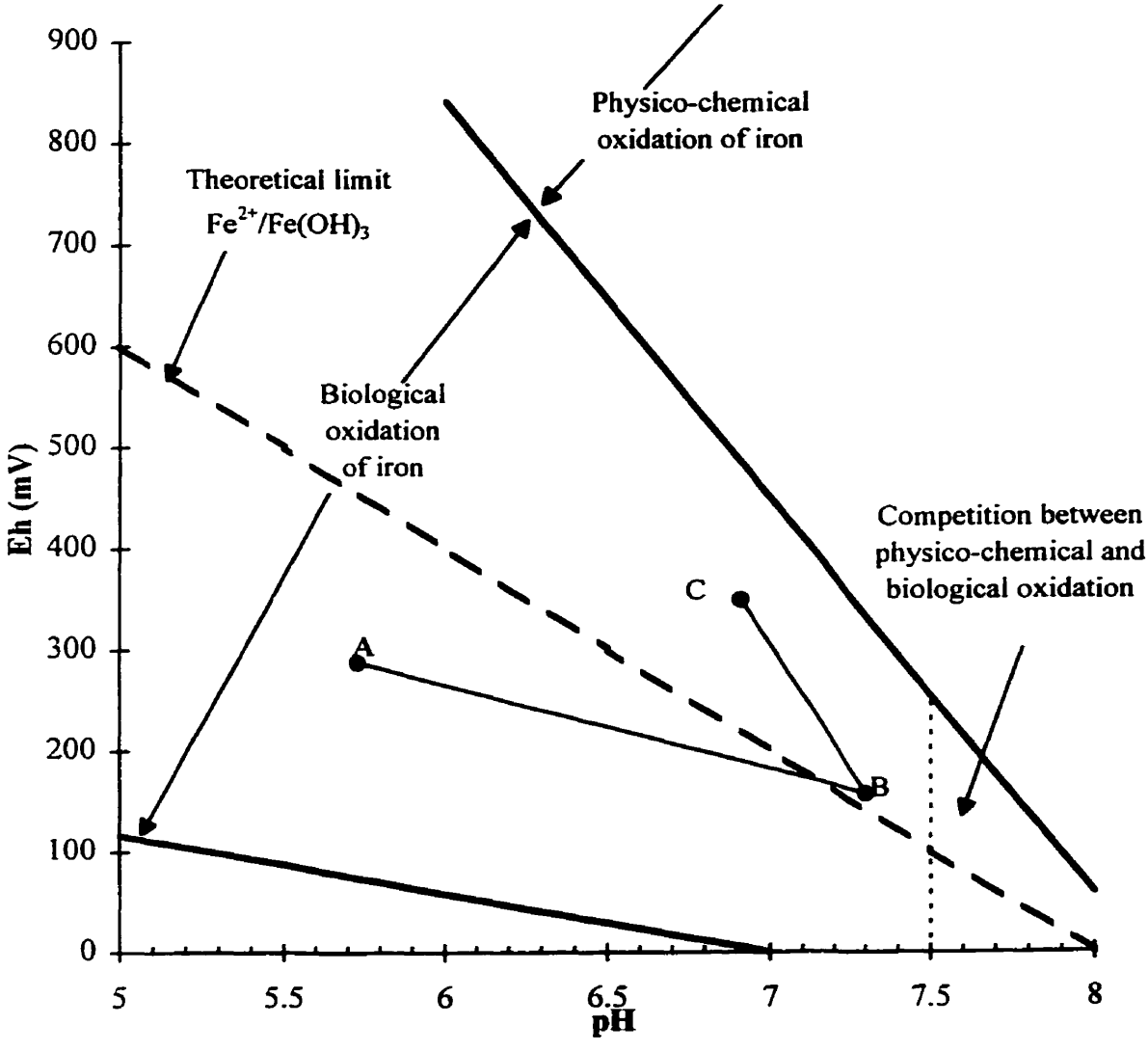

Figure 19. pH-Eh diagram indicating water conditions before and after primary filter (after Mouchet, 1992).

Thus it was thought that iron bacteria which are difficult to detect upon direct examination (Hanert, 1981b) were perhaps present, such as those from the Siderocapsaceae family. Therefore, the plant was operating in the transition area between biological and physico-chemical regimes. Because the operating conditions of the facilities could not be altered during the peak summer months, the pilot study was undertaken on site to verify biological treatment feasibility and if successful, to repeat the aeration-ORP trials on pilot scale.

From Figure 19, it is noted that as the pH increased from 5.7 to 7.3 with the addition of caustic soda, the Eh decreased from 290 to 160 mV. This is expected as pH and Eh have been shown to exhibit an inverse relationship (Heduit and Thevenot, 1989). Evidently, the change in iron concentration of the water was significant enough after passing through the filter that this ultimately produced an increase in Eh to approximately 350 mV.

Theoretically, the pH should not change across the filter. It is possible that the sampling point was too close to the point of caustic injection. Nevertheless, the aeration-ORP trials suggested that at least some physico-chemical oxidation was taking place and thus, the results could not be interpreted for evaluating ORP as an indicator in biological iron treatment.

4.2 Biological Pilot Study

4.2.1 Startup of pilot filter

After 16 days of operation under seemingly favourable conditions for a natural germination, the pilot was still not eliminating any iron. Because the raw water pH was slightly lower than recommended (Mouchet, 1992), a second trial to instigate growth was attempted by temporarily supplying the pilot with pre-filtered water from the plant (see Table 7 for chemical parameters). After filtering the higher pH water for approximately 20 hours, the pilot visibly contained a considerable amount of red precipitate, and the gauge pressure at the head of the column had increased to approximately 80 kPa (increase in pressure drop of 30 kPa). The filter was regenerated and the supply line changed back to the raw water.

The pilot was put back into operation with a reduced flowrate of 150 L/h, or a superficial velocity of 30 m/h, and column pressure regulated to 50 kPa. The evolution of TRI and ORP in the filtered water from the pilot, shown in Figure 20, took place over 122 hours of operation from September 9 to October 7, 1996. It appears from Figure 20 that a correlation exists between ORP and TRI and this is further discussed with results from the aeration-ORP trials below. Total residual iron was used, instead of dissolved residual iron, because it was observed that total iron was essentially in dissolved form at the exit of the filter and there was more data available of TRI than DRI. It should be noted that the pH of the filtered water was virtually unchanged from that of the raw water (pH 5.7).

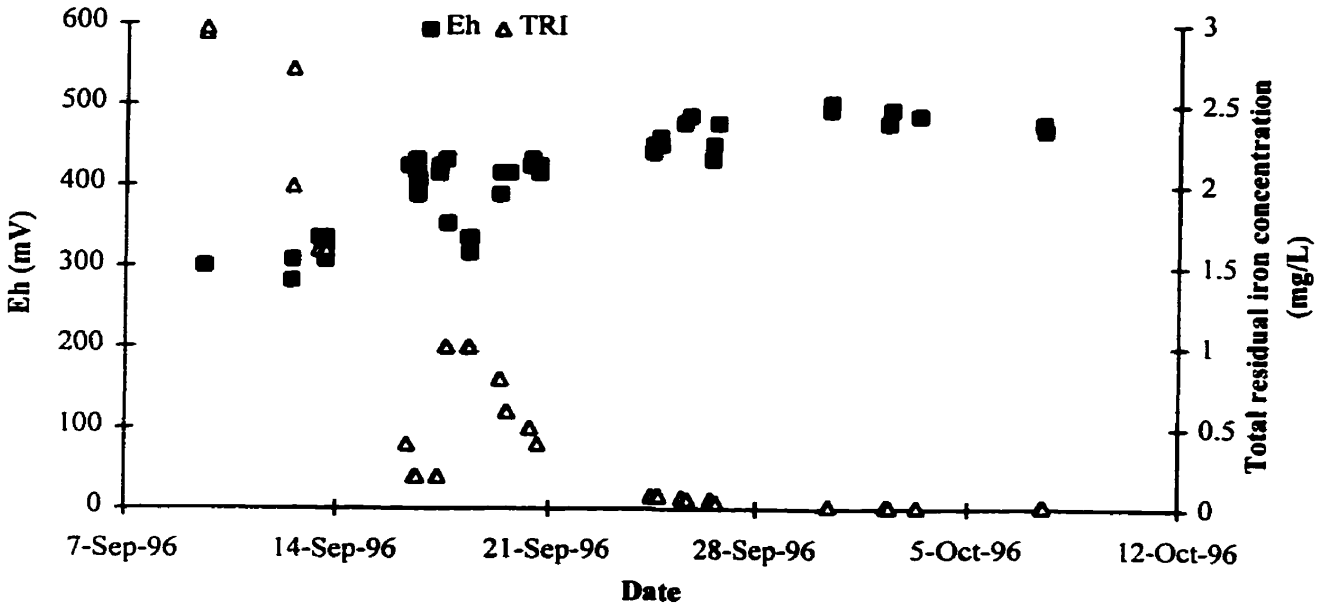

Figure 20. Startup of biological iron elimination on pilot scale.

4.2.2 Pilot filter backwash

Essentially, the backwash is expected to preserve the biomass while removing the sludge which progressively clogs the filter. During backwashing of the pilot column, this was gauged by visual inspection of the backwash water which should not become clear but rather retain a reddish-orange tint.

Two filter regenerations on pilot scale were carried out in September 1996 during startup, generally for the purposes of collecting samples of backwash sludge. The backwash at this time consisted of both water and air sent countercurrently (wash) through the column, followed by water alone (rinse). In October it was found that the

rinse portion of the backwash was carried out cocurrently on the full-scale filters and so the protocol for the pilot filter was changed to correspond to the full-scale facilities.

The flowrate and duration of the pilot backwash were also modified when it appeared that the filter required a lengthy maturation time (2 - 3 hours) before achieving relatively consistent residual iron concentration.

Samples of sludge collected in September and October from the pilot did not reveal the most common iron bacteria, *Gallionella* or *Leptothrix*, nor iron bacteria of the genus *Sidercapsa*. It should be noted that the Siderocapsaceae family of iron bacteria encompasses many genera which are said to be difficult to identify on direct examination. These bacteria are generally said to develop in environments where there is a source of organic carbon and a pH near neutral, which was not the case for the raw water at Seignosse. However, some Siderocapsaceae species have been observed in lower pH environments and exhibiting facultative autotrophy, which would make them potential candidates for the present system. The development conditions of the genus *Metallogenium* also make it a possibility. In any case, biological treatment can be strongly postulated as several performance factors attested to biological and not physico-chemical oxidation.

Firstly, the pH and Eh of the raw and filtered water were clearly in the region of iron bacteria activity when placed on Figure 9 or 19 (pH 5.7 was unchanged, Eh increased from 290 mV to 510 mV). Secondly, the velocity of filtration was typical for biological iron removal (30 m/h), whereas physico-chemical processes are usually restricted to a maximum rate of 15 m/h (Mouchet, 1992). Also, the effective size of sand in the pilot was 1.35 mm whereas physico-chemical oxidation requires sand between 0.5 and 1 mm

in size (Degrémont, 1991). And lastly, the residual iron was essentially all in dissolved form while previously there was a discrepancy between the total and dissolved forms of residual iron during the aeration-ORP trials on the primary filter.

4.2.3 Aeration-ORP trials

Once desirable conditions and satisfactory iron removal were established in the pilot, it was possible to carry out the aeration trials in early October. Because the gauge pressure in the column was only slightly elevated (70 kPa), the trials were initiated without first regenerating the filter. Figure 21 shows the evolution of DO, TRI and Eh over the 7 runs.

Despite the large variations in DO, the removal of iron was practically constant, as was the Eh, with the exception of run 2 where air injection was completely halted. At the very end of the trials, TRI increased suddenly from 0.005 to 0.330 mg/L, accompanied by a decrease in ORP from 500 to 390 mV. The filter had achieved saturation and a backwash was initiated. Thus the dramatic drop in ORP signaled the need for filter regeneration.

The trials revealed that an effective removal of iron can be achieved with a low level of dissolved oxygen (0.2 - 0.6 mg/L). A comparison of runs 1 and 2 shows the value of using ORP in contrast to DO to evaluate process reliability. In both cases, the DO levels are similar, 0.20 and 0.16 mg/L, respectively. However, the ORP is much higher in run 1, corresponding to excellent removal of iron. It should be noted that analyses indicated that TRI in the filtered water was essentially in dissolved form.

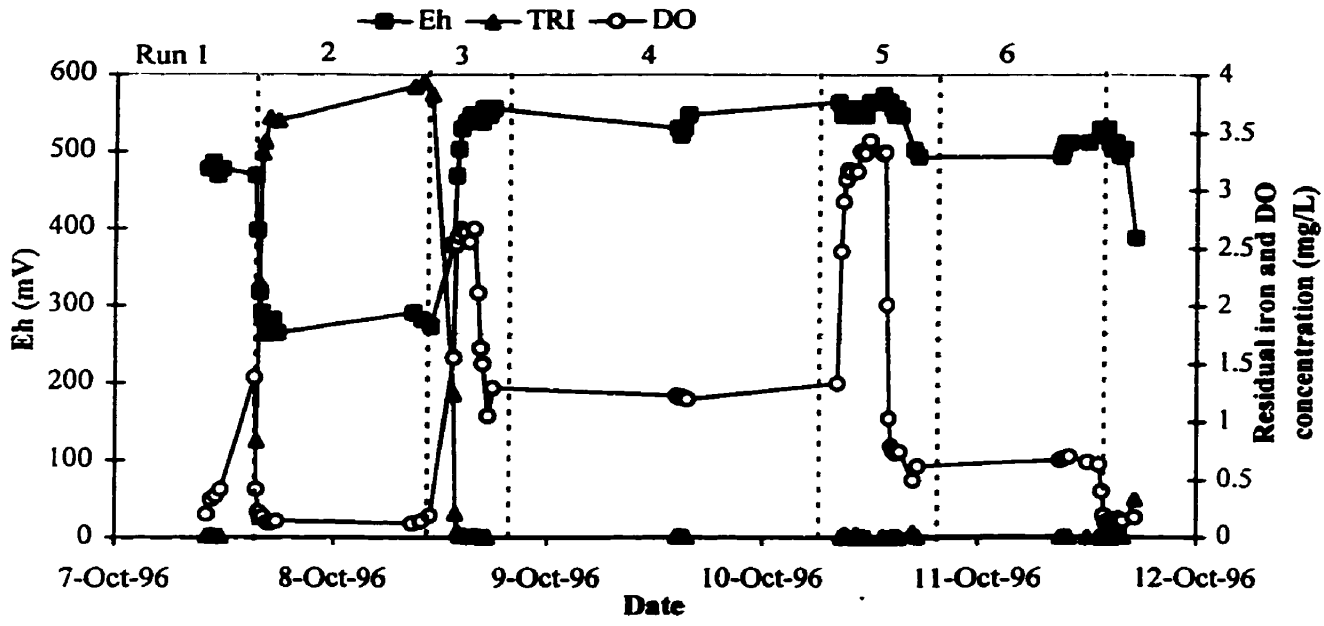

Figure 21. Results from the aeration-ORP trials on pilot-scale in October 1996.

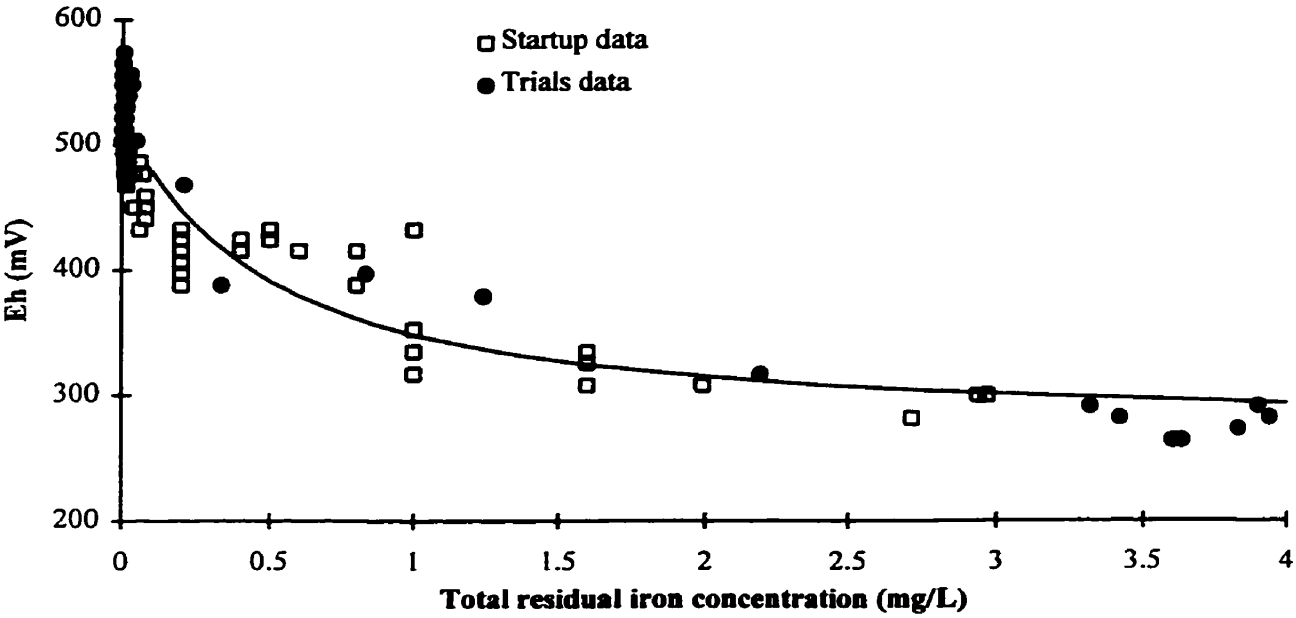

Figure 22. Correlation between ORP and TRI during start-up and trials on pilot-scale.

Several authors attest to the fact that physico-chemical oxidation of iron cannot take place at an appreciable rate when the pH is below neutral (Ehrlich, 1990; Mouchet, 1992). The implication of this statement for the present research is twofold. Firstly, it supports the presumption of biological action. Secondly, because the pH of the raw water studied was low, it would be theoretically possible to further increase the air injection without greatly influencing physico-chemical oxidation. Thus, the dissolved oxygen content could be increased to saturation level and there would be little to no competition for ferrous ions between biological and physico-chemical oxidation. Conversely, in biological processes where the raw water has a pH in the neutral range, increasing the DO level would possibly provoke some physico-chemical oxidation, such as was seen during the aeration-ORP trials on the primary filter in June. Thus, evaluating the effect of DO on biological iron treatment and controlling the air injection with ORP may be of greater importance for such facilities, in order to favour biological action.

As with the pilot start-up shown in Figure 20, it was possible to see a correlation between ORP and TRI concentration for the aeration-ORP trials shown in Figure 21. The data from Figure 21 was combined with the data from start-up of the pilot (Figure 20) to demonstrate the relationship between ORP and TRI as shown in Figure 22.

A non-linear regression between ORP and TRI was determined using Sigmaplot 4.0 software. The software rendered a correlation coefficient (R^2) of 0.8848. The relationship was modified to solve for total residual iron and is shown as follows.

$$[TRI] = \frac{Eh - a}{b - c(Eh)} \qquad \text{when } 300 < Eh < 470 \text{ mV} \qquad (17)$$

where [TRI] = total residual iron concentration in filtered water (mg/L)

Eh = standard oxidation-reduction potential of filtered water (mV)

a = constant, 525.603 mV

b = constant, 574.893 mV·L/mg

c = constant, 2.157 L/mg.

The regression model may be applied within upper and lower limits to predict TRI concentration for a given ORP measurement. The correlation appears to become ineffective at ORP levels greater than approximately 470 mV, where experimental results showed iron concentrations to be consistently below regulation limits. In addition, for values of ORP below approximately 300 mV, total iron levels were found to be consistently greater than or equal to 3 mg/L. Thus, for the present application of biological elimination of iron from drinking water, equation 17 can be used to predict total residual iron concentration for ORP levels between 300 and 470 mV.

4.3 Second Study on Full Scale

4.3.1 Primary filter startup without pH adjustment

Once the plant was no longer producing water for the water distribution network, it was possible to stop the injection of caustic soda (October 1996) in an attempt to develop the same performance as on the pilot. As soon as the filter began to operate without the pH adjustment, the residual iron content in the filtered water increased to approximately 1.10 mg/L and remained on the order of 1 mg/L for several cycles. During this time, it was noticed that pressure drop across the filter did not increase by more than 10 kPa

throughout a cycle, so it was proposed that the length of the cycle be increased from 500 m^3 to 1000 m^3.

In addition, visual inspection indicated that the backwash was not preserving enough of the bacterial mass to accomplish sufficient removal (backwash water was becoming clear). Thus, the duration of the air and water portion of the backwash was shortened from 5 minutes to 3 minutes.

These changes are shown in Figure 23 which encompasses approximately 169 hours of filter operation (3 cycles of 500 m^3 and 10 cycles of 1000 m^3) with a DO concentration of 1.0 mg/L. Towards the end of this period, primary filtered water had a consistent TRI concentration of 0.025 ± 0.007 mg/L and an Eh of 508 ± 9 mV.

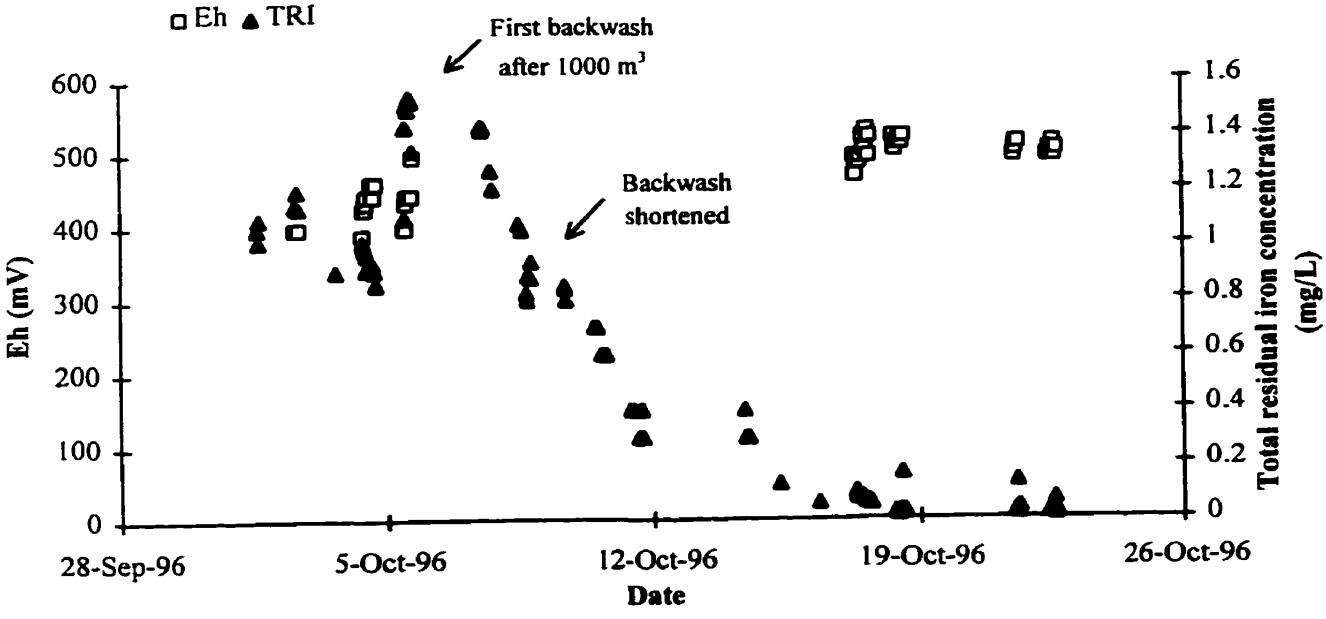

Figure 23. Primary filter start-up without pH adjustment in October 1996.

4.3.2 Biological treatment hypothesis

Since the pilot column and the primary filter were operating under approximately the same conditions in October, it was assumed that the same treatment mechanism was taking place in each. As discussed earlier, analysis of pilot sludge did not reveal the iron bacteria responsible for iron elimination though several factors supported biological activity. On-going study of the site is attempting to identify the micro-organisms present in the primary filter.

Another factor which supports the postulation of biological activity is the filter retention capacity. The iron retained during one filtration cycle is calculated with the following equation:

$$\frac{[TI]-[TRI]}{SA} \times V = C_R \qquad (18)$$

where $[TI]$ = total iron concentration in the raw water (g/m^3)

$[TRI]$ = total residual iron concentration in the filtered water (g/m^3)

SA = filter cross sectional area (m^2)

V = volume of water filtered in one cycle (m^3)

C_R = filter retention capacity (g/m^2).

Given that SA is 3.14 m^2 and V is 1000 m^3; and assuming a raw water iron concentration of 3.8 mg/L and a filtered water total residual iron concentration of 0.03 mg/L, C_R is calculated to be 1.20 kg/m^2. This value corresponds closely to the typical value of 1.25 kg/m^2 reported by Mouchet (1992) for biological filters having a superficial velocity of 30 m/h and containing sand of 1.18 mm effective size.

4.3.3 Summary on primary filter operation

Upon initial startup in 1990, the full-scale facilities were not immediately successful at iron removal. In fact, after several months of operation with only air injection, the primary filter was essentially not removing any iron. Finally, following a study on the site by P. Mouchet of Degrémont in March 1991 the pH adjustment was put into place (Mouchet, 1991). These results were communicated in an unpublished internal report which is contained in Appendix 2. Because the filter began to remove iron almost immediately, the pH adjustment by caustic soda was deemed necessary for reliable operation. Analyses of the backwash did not reveal the typical bacteria such as *Gallionella* or *Leptothrix* at the time, and Mr. Mouchet suggested that bacteria from the Siderocapsaceae family were possibly present, though this was never confirmed.

It should be recalled that analyses of sludge from the primary filter in June did not reveal any typical iron bacteria. However, the trials in June suggested that both biological and physico-chemical oxidation were taking place. Thus it is possible that some bacteria (i.e., from the Siderocapsaceae family) were present at the time, given the higher pH environment suited to both their development and the auto-oxidation of iron. Furthermore, poor filter operation (residual iron concentration above the French norm of 0.2 mg/L) could have been due to the shorter filtration cycles and longer backwashes which hindered bacterial development.

A comparison of previous and current operating conditions on the primary filter and iron treatment effected are shown in Table 8. As shown from the initial study on the full-scale plant in June 1996, the primary filter rarely eliminated more than 90 - 95% of

raw water total iron and filtered water usually contained greater than 0.20 mg/L of iron (French norm in drinking water). It is evident that the current operating conditions without the pH adjustment have led to more effective iron removal (98 - 99%) and savings in backwash water. A pH adjustment is still necessary in the final product to increase pH to approximately 7.6, the standard for potable water.

Table 8. Summary of previous and current operating conditions on the primary filter.

Parameter	June 1996	October 1996
Volume filtered per cycle	500 m^3	1000 m^3
Length of backwash (air+water)	5 min.	3 min.
Filtered water pH	6.9	5.7
Filtered water Eh	349 mV	500 mV
Raw water total iron	3.80 mg/L	3.80 mg/L
Total residual iron	0.339 mg/L	0.028 mg/L
Dissolved residual iron	0.130 mg/L	0.016 mg/L
% Total Iron Removed	91.1 %	99.3 %

The time of maturation after a backwash was evaluated a final time for the primary filter. Figure 24 shows the TRI to be well beneath the regulation standard for iron (0.20 mg/L) at the beginning of each of 3 cycles. Maturation time was observed to be approximately 15 minutes in each case. When compared with the maturation time of 100 minutes observed on the full-scale facilities in June 1996, it is evident that a more effective backwash was taking place in October. Furthermore, it was observed that the TRI was essentially constant at approximately 0.3 mg/L up to filter regeneration. Thus

no increase in TRI was seen towards the end of the cycle as compared to the primary filter results from June (recall Figure 14) where TRI attained up to 1.3 mg/L near the end of the cycle.

It should be noted that the secondary filter, intended for manganese removal, was not removing any manganese throughout the duration of the study. This was not of concern at the beginning of the summer, for the concentration of manganese in the raw water (Table 3) was consistently around 0.04 mg/L (below the French norm of 0.05 mg/L). However, over the course of the research, changes were noticed in raw water quality, notably in the manganese content.

Figure 25 indicates the manganese content increased significantly to 0.055 mg/L in September 1996. Still, at this time, the secondary filter was not eliminating any manganese. The raw water quality returned to 0.04 mg/L shortly afterwards but the problem remained of how to eliminate manganese in the case of future fluctuations in raw water quality. The operating modifications effected on the primary filter in October have enabled a satisfactory elimination of iron to take place, thus making the secondary filter available for changes in operating conditions to induce manganese removal.

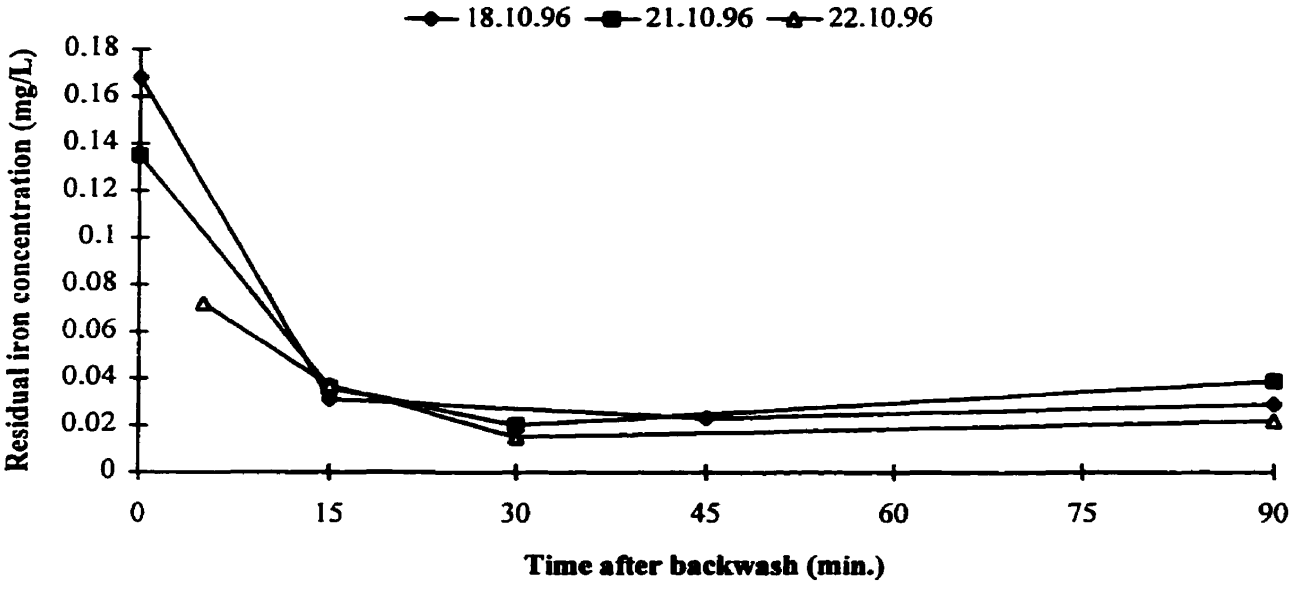

Figure 24. Primary filter maturation after 3 different backwashes, October 1996.

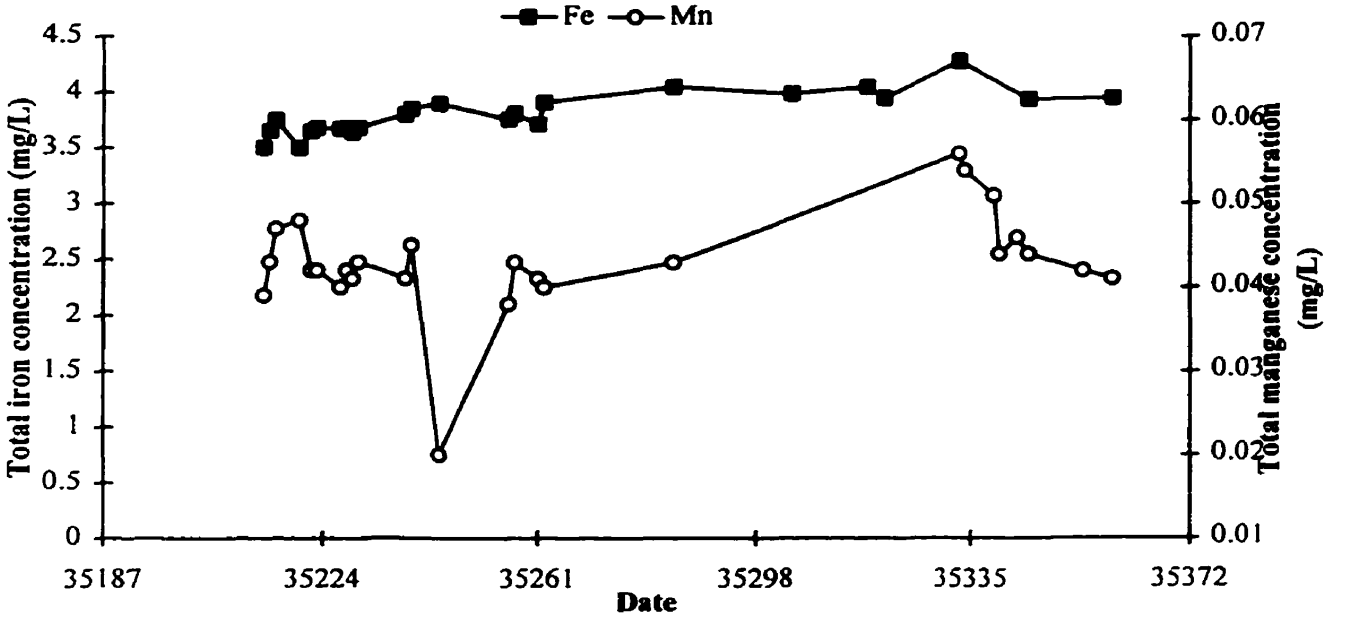

Figure 25. Iron and manganese content of raw water at Seignosse during study.

5. RESULTS AND DISCUSSION FOR SEPTMONTS

5.1 Biological Pilot Study

5.1.1 Startup of pilot filter

Upon arrival at the site of the biological pilot study in Septmonts, the pilot was operational and appeared to be functioning under biological conditions. Previous analysis of the sludge generated in the primary filter of the full-scale plant had revealed the common iron bacteria *Gallionella*. Since the pilot was essentially operating under the same conditions (air injection but no pH adjustment of raw water), it followed that the same activity was present in the pilot.

However, it was soon noticed that the column was not operating on a continuous basis, which led to variations in DO, TRI and DRI levels in the filtered water. The use of a separate pump to supply the column was the source of the problem, as each time the full-scale facilities began to operate, the water table level would descend from 9 m (static level) to 14 m (dynamic level) so as to result in no flow to the pilot. This occurred despite the fact that the pump supplying the pilot was situated at a depth of 14 m.

The use of a separate pump to supply the pilot meant that the pilot received raw water with variable total and dissolved iron content at the point when the full-scale facilities shut down. At the moment of plant downtime, the total iron content in the raw water (delivered to the pilot) increased to, for instance, 5.00 mg/L on November 20, 1996, while the dissolved iron content increased to 4.65 mg/L. Analyses performed one hour after plant shutdown on November 28th indicated raw water total iron concentration

had decreased to about 3.24 mg/L. Manganese content of the raw water was always in dissolved form.

The supply pump for the pilot column was lowered from its initial depth of about 14 m to 23 m in an attempt to rectify the problem. When this action failed to have an effect on pilot operation, a level indicator was installed on the open air tank at the exit of the pilot column in an effort to regulate flow from the column to the tank. This, too, did not keep the column from emptying during times of plant operation.

The remaining solution was to adjust the pump speed with each startup and shutdown of plant operation, in order to maintain flowrate to the column during experimentation. At the end of daily experimentation, it was also necessary to shut off the pump and close all valves exiting the column to prevent variations upon the following startup. Thus, it was possible to carry out the aeration-ORP trials on the biological pilot column.

5.1.2 Aeration-ORP trials

The aeration-ORP trials were initiated on the pilot during the month of November, once it was decided to regulate pilot operation manually. Flowrate was maintained at approximately 70 L/h or 14 m/h, which corresponded with plant operation. The ensemble of analyses performed are presented in Figure 26, showing the variation in Eh, DO and TRI in the filtered water for 7 runs.

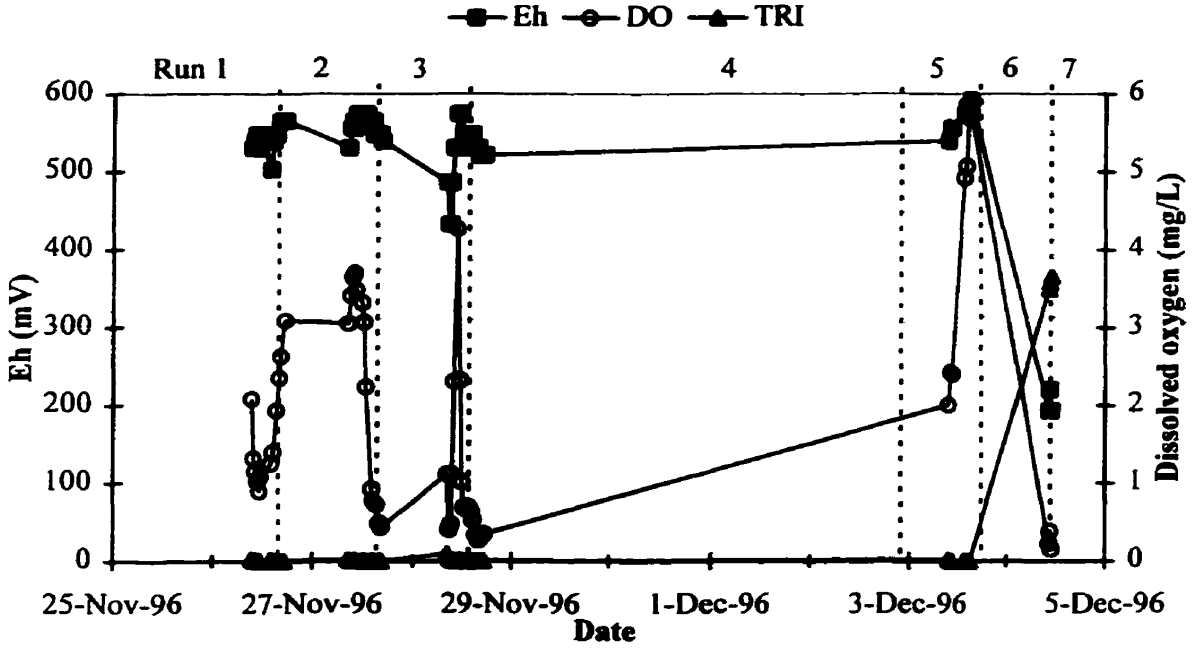

Figure 26. Results from the aeration-ORP trials on pilot scale, November 1996.

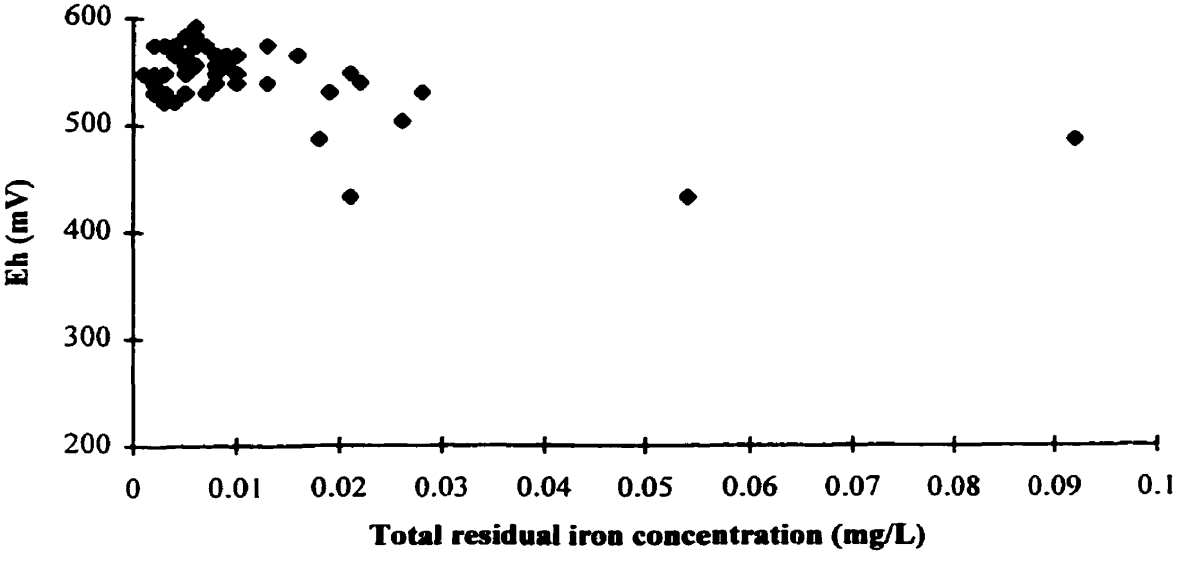

Figure 27. Relationship between ORP and TRI during aeration-ORP trials.

Each adjustment of pilot operating conditions (with plant startup or shutdown) still resulted in a minor upset to filtered water conditions. With the exception of the data from the final run where the air injection was halted, the concentration of TRI was consistently low (0.013 ± 0.016 mg/L) for the range of DO levels observed; and the mean Eh value recorded was 542 ± 33 mV. In the last run where air injection was zero, the mean TRI was 3.58 ± 0.08 mg/L, as reflected by a lower value of Eh (202 ± 16 mV). It was noticed that a similar relationship between Eh and TRI, as seen previously in Figure 22, likely also existed for the data at the present site. The resulting Eh and TRI values are plotted in Figure 27. Unfortunately, there was a significant lack of reliable Eh-TRI data points from the startup of the biological pilot (for Eh between 200 and 400 mV). Thus a good correlation between the two parameters could not be obtained.

It can be concluded from the above trials that Eh is a good indicator of iron removal. An ORP reading of 440 mV or higher indicates the TRI concentration is less than 0.1 mg/L. Also, a low level of dissolved oxygen concentration, on the order of 0.3 mg/L, is sufficient for effective removal of iron. The elimination of iron does not seem to be hindered nor improved by increasing the DO level.

5.1.3 Summary on the biological pilot study at Septmonts

Biological treatment of iron at Septmonts has revealed many of the same trends observed at the previous site. These include: a low level of dissolved oxygen is required to accomplish effective iron removal, the measurement of ORP appears to be a reliable indicator of iron concentration in the filtered water, and increases in DO level do not improve nor hinder filter operation.

In view of the similar level of DO that was required at both Seignosse and Septmonts, it is interesting to compare the two sites. A low level of DO (0.3 mg/L) was sufficient for effective biological iron removal in two raw waters: one with a pH of 5.7 and an Eh of 290 mV; and one with a pH of 6.7 and an Eh of 174 mV. Given the pH of a system, a certain DO concentration is required to increase the Eh to the level required for bacterial development. Thus, based on the fact that in the lower pH environment (Seignosse) the Eh was significantly higher, the same level of DO (0.3 mg/L) produced essentially the same effect as in the higher pH/lower Eh environment.

It can be recalled that while typical iron bacteria of the genus *Gallionella* were confirmed at Septmonts, the iron bacteria at Seignosse were not identified. And with the exception of the pH and Eh of the raw water and rates of filtration, the results from the two sites were quite similar, as shown in Table 9.

Table 9. Results from trials on biological pilots at Seignosse and Septmonts.

Parameters	**Seignosse**	**Septmonts**
Filtered water pH	5.7	6.7
Filtered water Eh	522 mV	538 mV
Raw water total iron	3.80 mg/L	3.82 mg/L
Total residual iron	0.017 mg/L	0.014 mg/L
Dissolved residual iron	0.015 mg/L	0.014 mg/L
% Total iron removed	99.6 %	99.6 %
Average flow rate	150 L/h	70 L/h
Total time of filtration	34 hours	36 hours
Filter retention capacity	3.9 kg/m^2	1.9 kg/m^2

The results from the aeration-ORP study at each site (not including runs when air injection was zero) are used to compare the two sites, since regular analyses were carried out for the trials and reliable average values could be obtained. It is observed that the retention capacity (recall equation 18) was twice as high at Seignosse than at Septmonts. However, this appears to be due to the difference in flow rates at the two sites, which are also related by a factor of about two. Other parameters relevant to equation 18 are approximately equivalent: pilot cross-sectional area (0.005 m^2), total time of filtration, and average difference between inlet and outlet concentrations of iron ([TI] - [TRI]). The retention capacities shown in Table 9 also represent values typical to biological iron treatment [2 to 5 kg/m^2 (Mouchet, 1992)].

5.2 Catalytic Pilot Study

As previously mentioned, elimination of fines on the two materials was the first required step before experimentation. This was a lengthy process in the case of *Purolite* and analyses began even though fine black particles were still escaping with the filtered water.

5.2.1 Ferrolite MC2

After two hours of fines removal, normal operation commenced on the *Ferrolite MC2* column at a medium flowrate (12 m/h) and low air injection. The first run shown in Table 10, along with raw water conditions, indicates excellent removal of both total and dissolved iron and some removal of manganese. After 5 hours of operation at the initial conditions, the manganese concentration increased and soon exceeded the raw water content. Thus the catalytic material seemed to be interfering with the manganese content

of the filtered water. Elimination of iron continued to be satisfactory and appeared to be indicated by a high ORP (510 mV).

Table 10. Startup of the *Ferrolite MC2* pilot: Raw and filtered water parameters.

Parameters	**Mean values ± Std.Dev.**	
	Raw water	**Filtered water**
pH	6.70 ± 0.06	6.60 ± 0.05
Eh (mV)	174 ± 27	510 ± 24
Dissolved oxygen (mg/L)	0.16 ± 0.11	0.26 ± 0.04
Total iron (mg/L)	3.82 ± 0.82	0.010 ± 0.005
Dissolved iron (mg/L)	3.47 ± 0.74	0.004 ± 0.003
Total manganese (mg/L)	0.317 ± 0.019	0.132 ± 0.018

The ensuing experiments involved analyses at various combinations of high and low air injections, coupled with high and low velocities of filtration. The results are summarized in Table 11. Dissolved residual iron (DRI) and dissolved residual manganese (DRM) are indicated to evaluate the oxidation capacity of the material and these values can be compared with raw water concentrations shown in Table 10. It should be noted that total manganese in the raw water was completely in dissolved form.

Even though *Ferrolite MC2* seemed to eliminate total iron quite well in the first run of Table 11 (which corresponds to the startup conditions shown in Table 10), as soon as the air injection was increased (run 3), air bubbles significantly disturbed the filter bed, causing a surge of fine particles with the flow exiting the column. Therefore, the dissolved iron (or manganese) gave the best indications of oxidation occurring. An ORP

reading above 500 mV was a good indication of iron oxidation taking place at nearly 100% efficiency. In total, the *Ferrolite MC2* pilot filtered 1457 L of raw water.

Table 11. Iron and manganese oxidation on *Ferrolite MC2*.

Run	Velocity (m/h)		Dissolved oxygen (mg/L)		DRI (mg/L)	DRM (mg/L)	Eh (mV)
1	medium	12	low	0.26 ± 0.04	0.004 ± 0.003	0.112 ± 0.010	510 ± 24
2	high	15	none	0.11 ± 0.11	0.002 ± 0.001	> 0.770	503 ± 13
3	high	15	high	4.22 ± 0.11	0.000	> 0.770	594 ± 5
4	low	5	low	0.52 ± 0.16	0.000	> 0.770	519 ± 8
5	low	5	high	6.69 ± 0.07	0.000	> 0.770	543 ± 26

Ferrolite MC2 appears to function well in the oxidation of iron at both low and high velocities and equally well for high and low levels of DO. Oxidation of manganese at approximately 65% efficiency occurred in the first 5 hours of operation (300 L) after which point the filter was producing water with more manganese than the raw water. Thus, it would be necessary to regenerate with potassium permanganate either on a frequent or continual basis for this material to function continually.

5.2.2 Purolite

After several hours of fines removal, analysis finally began on the water filtered by the second catalytic material, *Purolite*. At a medium flowrate (12 m/h) and low air injection (1.07 ± 0.59 mg/L) the column was found to eliminate nearly 100% of both the total and dissolved iron. Some manganese (total and dissolved) was also removed.

Table 12 summarizes the oxidation of iron and manganese by *Purolite* at various levels of DO and velocities of filtration. Initial conditions in the raw water can be referred to in Table 10.

Table 12. Iron and manganese oxidation on *Purolite*.

Run	Velocity (m/h)		Dissolved oxygen (mg/L)		DRI (mg/L)	DRM (mg/L)	Eh (mV)
1	medium	10	low	1.07 ± 0.59	0.000	0.101 ± 0.015	548 ± 12
2	medium	10	high	3.87 ± 0.22	0.000	0.093 ± 0.007	580 ± 9
3	low	4	low	1.68 ± 0.20	0.000	0.106 ± 0.026	590 ± 9
4	low	5	none	0.09 ± 0.05	0.000	0.085 ± 0.008	498 ± 13
5	high	20	none	0.12 ± 0.04	0.000	0.089 ± 0.020	512 ± 16
6	low	5	high	4.56 ± 1.09	0.000	0.080 ± 0.003	570 ± 16

Oxidation of iron was exceptional on the catalytic material *Purolite*. Furthermore, 66 - 75% of manganese was oxidized up to a velocity of 20 m/h and without the filter requiring regeneration. This performance was observed throughout experimentation on *Purolite*, during which time the filter processed approximately 1127 L of water. As with the *Ferrolite MC2*, a redox potential greater than approximately 500 mV indicated that 100% of iron was being oxidized.

5.2.3 Summary on the catalytic pilot study

The catalytic materials *Ferrolite MC2* and *Purolite* were investigated in pilot columns with an upward flow configuration which resulted in particulate matter escaping with the filtered water. Therefore, the apparent removal capacity of the two materials tested was not determined. However, the oxidation capacity of each was shown to be excellent for iron, which seemed to be reflected by an ORP greater than 500 mV in both cases.

The performance of each material is further evaluated for the total volume of water filtered per mass of catalytic material when oxidation of iron (manganese) was consistent. The total mass of *Ferrolite MC2* is calculated from the bulk density (1120 kg/m^3) and the dry volume occupied in the column (1.2 m × 0.005 m^2) to be 6.72 kg. Thus *Ferrolite MC2* filtered 1457 L or 217 L/kg and consistently oxidized iron at 100%. In terms of manganese oxidation at 65%, *Ferrolite MC2* filtered 300 L or 45 L/kg before reaching saturation.

Similarly, *Purolite*, (bulk density 1370 kg/m^3) with a total mass of 8.22 kg, filtered 1127 L or 137 L/kg while consistently oxidizing iron at 100% and manganese at 75%.

Based on the results from the pilot study at Septmonts, the catalytic material *Purolite* gave a superior performance to *Ferrolite MC2*.

6. CONCLUSIONS

Biological iron removal for potable water production was investigated on pilot-scale and full-scale facilities. From the investigation of iron treatment on two pilot columns at two sites (Seignosse and Septmonts), it was observed that the measure of oxidation-reduction potential (ORP) appears to be a good indicator of changes in iron concentration in the filtered water of a biological process. A system-specific minimum value of ORP can be determined which corresponds to a maximum acceptable level of iron in the filtered product. Thus, any measure of ORP which falls below the system-specific minimum value would indicate perturbations in iron treatment which could be due to, for instance, filter saturation.

The effect of varying the dissolved oxygen (DO) content of the raw water was also explored for its impact upon the biological iron removal process and the ORP measurement. It was perceived that for the raw waters examined (pH 5.7 and pH 6.7), an increase in DO content above the minimum requirement did not improve nor hinder the biological treatment of iron. This observation is consistent with literature which indicates that for a pH below neutral, physico-chemical oxidation is not significant and does not compete with biological oxidation, regardless of the DO concentration (Ehrlich, 1990; Mouchet, 1992). In addition, the variations in DO did not produce a quantifiable response in ORP above the minimum required DO concentration.

Based on the results from the pilot at Seignosse, operating conditions of the full-scale primary filter at the site were altered (no pH adjustment of the raw water, decreased frequency and length of backwash) to produce improved treatment of iron and savings in

backwash water. The operating modifications were significant since iron treatment was made possible in a biological filter operating at a pH of 5.7, which was previously considered infeasible.

Samples of sludge collected in September and October from the pilot plant at Seignosse did not reveal the most common iron bacteria, *Gallionella* or *Leptothrix*, nor iron bacteria of the genus *Siderocapsa*. On-going study of the site is attempting to identify the micro-organisms present in the primary filter. Biological treatment can be postulated as several performance factors attested to biological and not physico-chemical oxidation. These included: pH and Eh of the raw water (5.7, 290 mV), velocity of filtration (30 m/h), effective size of sand in the pilot and primary filter (1.35 and 1.18 mm), residual iron concentrations in dissolved form, and filter retention capacities on the pilot and primary filter of 3.9 and 1.2 kg/m^2, respectively.

In general, it was found that the frequency and duration of the backwash are significant factors which affect the biological filter. Thus, the measure of ORP can be very useful as an indicator of the point at which filter regeneration is required. In future related studies ORP could be investigated as an indicator in determining the optimum times of the backwash and rinse of the filter (recall that the backwash consists of raw water and air sent countercurrently through the filter whereas the rinse portion is raw water alone sent cocurrently). Thus, for various finite backwash sequences, the ORP could be measured in the filtered rinse water to establish the minimum required rinse duration corresponding to the backwash. Such an investigation would permit the minimizing of filter maturation time, while maximizing the filtration cycle with respect to filter regeneration.

The oxidation capacities of two catalytic materials, *Ferrolite MC2* and *Purolite*, were evaluated under site-specific conditions. The raw water tested contained approximately 3.47 mg/L of dissolved iron and 0.317 mg/L of dissolved manganese. Both materials oxidized iron at 100% efficiency throughout the entire time of the trials regardless of DO concentration and for velocities up to 15 m/h on *Ferrolite MC2* and 20 m/h on *Purolite*. ORP measurements which were invariably greater than 500 mV during the trials seemed to reflect the consistent oxidation of iron observed. *Ferrolite MC2* filtered a total of 1457 L or 217 L per kg of catalytic material while consistently oxidizing iron at 100%. With respect to manganese oxidation at 65%, *Ferrolite MC2* filtered 300 L or 45 L/kg. *Purolite* filtered a total of 1127 L or 137 L per kg of catalytic material while consistently oxidizing iron at 100% and manganese at up to 77%.

The two catalytic materials were investigated in pilot columns with an upward flow configuration. Thus it was not possible to determine the filtration retention capacity of *Ferrolite MC2* and *Purolite*. Nevertheless, initial analyses of filtered water showed that both materials eliminated both total and dissolved species from the outset of the investigation. It was only when the air injection to the raw water was introduced that the filter bed was significantly disturbed. Therefore, it is recommended that a gravitational flow configuration be adopted for any future studies with these materials if air injection is to be used. In addition, because *Ferrolite MC2* achieved saturation with respect to manganese oxidation after filtering 45 L/kg, it appears that it would require regeneration with potassium permanganate on a continual or frequent intermittent basis.

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APPENDIX 1:

RAW WATER ANALYSES AT SEIGNOSSE, JULY 1996.

LYONNAISE DES EAUX
LABORATOIRE DE LA D.R.
AV DE CAMBO 64600 ANGLET

ANALYSE DE CONTROLE N° 719

Prélèvement effectué le : 01/07/96 par : AGENT DU SECTEUR

Commune de.....: SEIGNOSSE

Lieu de prélèvement.....: SEIGNOSSE BOURG USINE FORAGE E4 EAU BRUTE

Nature du prélèvement...: RESSOURCE

Résultat transmis le....: 10/07/96 Type d'analyse : PA3

	RESULTATS	UNITES
Paramètres Organoleptiques.....:		
ASPECT	CLAIR	
COULEUR	<2.5	MG/L PT/CO
TURBIDITE	0.34	N.T.U
ODEUR	0	TX DILU.
ODEUR DETECTEE	/	
Paramètres Physico-chimiques.....:		
TEMPERATURE	13.8	DEG.C
PH SUR PLACE	6.10	
IS A LA TEMPERATURE DU PRELEVEMENT	-4.64	
CONDUCTIVITE A 20°C	142	µ.S/CM
CHLORURES (TITRIMETRIE)	29.5	MG/L CL
SULFATES (NEPHELOMETRIE)	4.5	MG/L SO4
CALCIUM (COMPLEXOMETRIE)	4.5	MG/L CA
MAGNESIUM (COMPLEXOMETRIE)	2.8	MG/L MG
SODIUM (AA FLAMME)	17.7	MG/L NA
POTASSIUM (ICP)	1.1	MG/L K
ALUMINIUM (COLORIMETRIE)	0.07	MG/L AL
DURETE TOTALE (COMPLEXOMETRIE)	2.3	DEG.F.
TITRE ALCALIMETRIQUE COMPLET (TITRIMETRIE)	1.6	DEG.F.
CARBONATES (CALCUL)	0	MG/L
HYDROGENOCARBONATES (CALCUL)	19.50	MG/L
ANHYDRIDE CARBONIQUE LIBRE	28.60	MG/L CO2
Substances Indésirables.....:		
NITRATES (TECHNICON)	<0.5	MG/L NO3
NITRITES (TECHNICON)	<0.05	MG/L NO2
AMMONIUM (COLORIMETRIE)	0	MG/L NH4

LYONNAISE DES EAUX
LABORATOIRE DE LA D.R.
AV DE CAMBO 64600 ANGLET

ANALYSE DE CONTROLE N° 726

Prélèvement effectué le : 01/07/96 par : AGENT DU SECTEUR

Commune de.....: SEIGNOSSE

Lieu de prélèvement.....: SEIGNOSSE BOURG USINE FORAGE E4 EAU BRUTE

Nature du prélèvement...: RESSOURCE

Résultat transmis le....: 10/07/96 Type d'analyse : B2A

	RESULTATS	UNITES
Paramètres Microbiologiques.....:		
COLIFORMES TOTAUX (MF)	0	/100ML
COLIFORMES THERMOTOLERANTS	0	/100ML
STREPTOCOQUES FECAUX (MF)	0	/100ML
DENOMBREMENT DES GERMES TOTAUX 37 DEG.C	13	/ML
DENOMBREMENT DES GERMES TOTAUX 22 DEG.C	82	/ML

CONCLUSION : LES RESULTATS DES PARAMETRES ANALYSES SONT CONFORMES AUX LIMITES DE QUALITE DES EAUX BRUTES POUR LA PRODUCTION D'EAU DESTINEE A LA CONSOMMATION HUMAINE.

Le 10/07/96, LE RESPONSABLE DU LABORATOIRE

ANALYSE DE CONTROLE N° 719

Prélèvement effectué le : 01/07/96
Commune de.....: SEIGNOSSE
Lieu de prélèvement.....: SEIGNOSSE BOURG USINE FORAGE E4 EAU BRUTE

	RESULTATS	UNITES
OXYDABILITE KMNO4 A CHAUD MILIEU ACIDE	0.47	MG/L O2
FER (COLORIMETRIE)	3500	MICROG/L FE
FER DISSOUS	2700	MICROG/L
MANGANESE (COLORIMETRIE)	60	MICROG/L MN
MANGANESE DISSOUS	60	MICROG/L MN

CONCLUSION : LES RESULTATS DES PARAMETRES ANALYSES SONT CONFORMES AUX LIMITES DE QUALITE DES EAUX BRUTES POUR LA PRODUCTION D'EAU DESTINEE A LA CONSOMMATION HUMAINE. EAU AGRESSIVE.

Le 10/07/96, LE RESPONSABLE DU LABORATOIRE

APPENDIX 2:

DEFERRISATION BIOLOGIQUE DE SEIGNOSSE: RAPPORT DE LA VISIT EFFECTUÉE LES 21 ET 22 MARS 1991.

DEPARTEMENT DES LANDES

oOo

DGA090B02E

oOo

DEFERRISATION BIOLOGIQUE DE SEIGNOSSE

oOo

RAPPORT DE LA VISITE EFFECTUEE LES 21 et 22 MARS 1991

Nous avons ausculté cette station, avec M. DUPUIS et J.L. PICCIRILLI.

La station était à l'arrêt à notre arrivée. Nous l'avons d'abord remise en service dans les conditions d'essais antérieurs, c'est-à-dire à débit réduit et sans contre-pression (évacuation de l'eau filtrée à l'égout). Les paramètres de fonctionnement étaient alors :

Q eau = 43,5 m3/h (rappel : Q nominal = 75 m3/h)

Pression amont = 0,6 b

Q air = 2,5 Nm3/h ($\frac{\text{Q air}}{\text{Q eau}}$ = 5,75 %)

...

Résultats après 1 heure de fonctionnement

		Eau Brute	Eau Filtrée
Température	(°C)	14	14
pH		5,7	5,7
Eh	(mV/H_2)	+ 60 mV (stabilisation difficile	-
O_2	(mg/l)	absence	1,4
NH_4	(mg/l)	0,05	0,05
NO_2	(mg/l)	0,03	0,02
Fer	(mg/l)	3,3	2,8
Manganèse	(mg/l)	0,02	0,02
rH		13,5	-
TAC	(°F)	2,2	2,2

L'augmentation du débit d'air à 3,8 Nm3/h ou 8,75 % du débit d'eau, élève la concentration en O_2 dissous à 2,8 mg/l mais ne change pas la teneur en fer résiduel dans l'eau filtrée.

Premières conclusions

- les seuls problèmes posés par cette eau sont le fer et l'agressivité carbonique ; en revanche, pas de problème de manganèse, NH_4, NO_2.
- les premières analyses, effectuées par le Laboratoire Départemental de Mont-de-Marsan en 1988, mentionnaient un pH de 6,8 (5.8.88) à 6,9 (2.11.88).

...

A la mise en service (été 90), le pH (mesuré sur place) était de 6,3, puis s'est abaissé progressivement pour se fixer maintenant à 5,6/5,7. C'est une valeur de pH que nous n'avons pas encore constaté en déferrisation biologique et qui d'ailleurs ne peut pas correspondre à une précipitation totale du fer, comme nous le verrons plus loin.

****

Trois heures après la remise en service, nous avons mis la station sous pression, à une valeur proche de la future pression de service lorsqu'elle refoulera dans le réseau ; cette mise sous pression a été obtenue en fermant partiellement la vanne de "rinçage" (utilisée pour la maturaton du filtre après lavage) qui est placée sur la tuyauterie de vidange par où s'écoule actuellement l'eau filtrée. Les paramètres de fonctionnement sont devenus :

Q eau = 36 m3/h

Pression amont = 4,6 b

Q air = 4,5 Nm3/h ($\frac{\text{Q air}}{\text{Q eau}}$ = 12,5 %)

Résultats après 3 heures de fonctionnement

		Eau Brute	Eau Filtrée
pH		5,65	5,65
Eh	(mV/H_2)	+ 80 mV	+ 335 mV
O_2	(mg/l)	absence	3,2
Fer	(mg/l)	3,3	2,6

...

Conclusions

- A ce pH, malgré un rapport air/eau théoriquement favorable à une bonne oxygénation de l'eau, le pourcentage de saturation en O_2 dans l'eau filtrée dépasse à peine 30 %.

- Le pH et le potentiel Redox auxquels on parvient dans l'eau filtrée ne correspondent pas encore à une précipitation totale du fer (voir fig. I, où le point 1 est représentatif de l'eau brute et le point 2 de l'eau aérée et filtrée).

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Le débit d'air a été ensuite porté à 5,9 Nm3/h. Le rapport Q air/Q eau était alors de 16,85 % (Q eau = 35 m3/h).

Résultats 2 heures après la modification

		Eau Brute	Eau Filtrée
pH		5,65	5,65
Eh	(mV/H_2)	+ 80 mV	+ 340 mV
O_2	(mg/l)	absence	3,75
Fer	(mg/l)	3,5	2,7

Sept heures après la modification, les résultats restaient inchangés.

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Conclusion

A un tel pH, la déferrisation biologique semble impossible.

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Nous avons alors mis en service la pompe de soude, qui venait d'être installée pour relever le pH de l'eau brute.

Avec un pH réglé à 6,9, nous avons voulu laver le filtre pour commencer un nouveau cycle de filtration ; l'ouverture de la vanne placée sur la tuyauterie d'évacuation des eaux de lavage a malheureusement provoqué un coup de bélier qui a cassé cette tuyauterie, en PVC. Il n'était donc plus question de laver le filtre sous peine d'inonder la station, et l'essai à continué avec un filtre qui avait successivement fonctionné dans des conditions très acides, puis très alcalines, et il reste donc une certaine incertitude sur les résultats qui vont être exposés dans ce qui suit.

La bonne valeur de pH a été obtenue le 23 mars en début d'après-midi, dans les conditions de fonctionnement suivantes :

Q eau : 35 m3/h

Pression amont = 4,6 b

Q air = 7,1 Nm3/h ($\frac{Q\ air}{Q\ eau}$ = 20 %)

		Eau Brute	Eau Filtrée
pH		5,6	6,9
Eh	(mV/H_2)	+ 70 mV	+ 350 mV
O_2	(mg/l)	absence	10,2 mg/l (= 100 % saturation)
TAC	(°F)	2,1	5,4

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L'augmentation de TAC correspond à un taux de traitement en soude, avant filtration, de 26,5 g/m3 (en NaOH pure), soit encore 2,3 l/h de lessive de soud à 400 g/l pour 35 m3/h d'eau brute.

Evolution des teneurs en fer (en mg/l)

Heure	Eau Brute	Eau Filtrée
15 h	3,2	1,6
16 h 30	3,0	1,1
17 h 30	3,1	0,3

Conclusions

La déferrisation biologique semble donc démarrer spontanément lorsque l'eau est mise dans des conditions de pH légèrement inférieures à 7, ce qui la place dans des conditions de précipitation totale du fer (concrétisées par le point 3 sur la figure I). Il subsiste toutefois de nombreuses incertitudes :

- confirmation du bon résultat qui a été obtenu le 23 mars en fin de journée, lorsque le filtre aura été remis en service après lavage ;

- vérification que cette évolution aboutit bien à une eau traitée totalement exempte de fer (il n'a pas été possible d'attendre ce résultat le 23 mars) ;

- si la voie biologique est confirmée, s'agit-il de bactéries indigènes ou de germes subsistant des précédents ensemencements ? J'ai cherché, au microscope, d'éventuelles ferrobactéries dans les écumes qui se forment spontanément à la surface de l'eau dans les tranchées d'infiltration qui reçoivent les eaux de lavage des filtres (et, actuellement, qui reçoivent aussi l'eau filtrée tant qu'elle n'est pas refoulée sur le réseau) : il en existe de très rares

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exemplaires (filamenteuses ou Gallionella), en quantité insuffisante pour en tirer une conclusion positive ; en revanche on peut y voir des très nombreuses bactéries libres, et en outre le floc ferrique observé dans ces écumes présente l'aspect d'un précipité formé par voie biologique ; il pourrait donc très bien y avoir prédominance d'autres espèces de ferrobactéries, comme le genre Siderocapsa qui ne forme ni gaine ni pédoncules ;

- enfin, et surtout, si tout ce qui précède est positif, vérification de la faisabilité du process au débit nominal de la station, c'est-à-dire 75 m3/h (soit v = 24 m/h).

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Conclusions générales

1. Sur cette eau, on ne peut espérer obtenir un bon résultat qu'en élevant le pH à une valeur approximativement comprise entre 6,6 et 7. Cette contrainte n'implique que la dépense d'une pompe doseuse supplémentaire, mais n'augmente pas la consommation globale en réactif puisque le taux de traitement final, pour le relèvement du pH de l'eau traitée, se trouvera diminué de la quantité déjà introduite dans l'eau brute.

2. Nous envisageons de poursuivre la mise au point de la station de la façon suivante :

   - éventuellement, ensemencement du sable avec les écumes collectées dans les tranchées de réception des eaux de lavage,

   - mise en place d'un débitmètre d'air gradué de 0 à 10 Nm3/h sous 5,5 b ;

   - réparation de la tuyauterie d'évacuation des eaux de lavage que nous remplacerons par une tuyauterie en acier ;

   - mise en place d'un circuit définitif d'injection de la soude dans l'eau brute (en remplacement du tuyau provisoire actuellement en place) ;

   - après lavage du filtre, redémarrage dans les conditions de fonctionnement du 23 mars après-midi (P = 4,5 b ; Q = 35 à 40 m3/h ; pH = 6,9 ; O_2 voisin de 100 % sat.) ;

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- si les résultats sont bons, affinage des paramètres de fonctionnement :

  * proportion minimale air/eau pour obtenir 90 à 100 % de la saturation en O_2 dissous sous la pression de service ;

  * définition de la zone de pH dans laquelle la déferrisation biologique atteint sa pleine efficacité et du pH mini à respecter impérativement

- si on a pu obtenir un cycle satisfaisant à demi-débit, passage à plein débit après lavage du filtre (pas de décolmatage ; 45 sec. soufflage ; 1 min. de rinçage, à augmenter éventuellement plus tard, si les résultats sont bons, jusqu'au temps nécessaire pour renouveler la tranche d'eau sale au-dessus du sable, ce qui devrait représenter environ 2 minutes) ;

- en cas de résultats insuffisants, (au cas où cette eau, dont le caractère inhabituel pour une déferrisation biologique n'a été révélé qu'à la mise en service, ne contiendrait pas assez de germes de bactéries du fer dont le domaine d'existence ne correspond que pour sa limite la plus extrême, aux caractéristiques chimiques actuellement mesurées) à demi-débit ou à plein débit, procéder à nouveau à un ensemencement avec les boues d'une autre station.

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