Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2009 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2009.918

12 (2009) 162–168

Colloidal iron and manganese in water affecting RO operation

Robert Y. Ning

King Lee Technologies, 8949 Kenamar Drive, Bldg. 107, San Diego, CA, 92121, USA
Tel.+1 (858) 693-4062; Fax +1 (858) 693-4917; email: Rning@kingleetech.com

Received 14 November 2008; Accepted 22 September 2009

ABSTRACT

The finding of various forms of iron, and less commonly of manganese, in numerous reverse osmosis (RO) membrane autopsies we have performed, have led us to call attention to the diverse forms of iron and manganese species in natural waters. Correlation of elemental composition analyses of foulants with contaminants in RO feedwater and pretreatment steps led to successful solutions of fouling problems by the modification of pretreatments, such as substitution of oxidation filtration strategies for iron and manganese reduction with sequestration with appropriate antiscalants. Cases where iron and manganese fouling failed to respond to sequestration with antiscalants, the existence in the RO feedwater of pre-existing colloidal iron and manganese particles are suspected. To fully control such fouling, speciation of the different forms of iron and manganese that exist in natural, industrial and wastewaters are central to process design, troubleshooting and RO system operation and maintenance. We have undertaken a literature review of iron and manganese colloidal chemistry as it pertains to the RO membrane process. This paper reviews the background for the association of iron with manganese in water treatment, natural sources of colloidal iron and manganese, early works on methods for the reduction of iron and manganese in traditional municipal waterworks where colloidal particles may be formed and not removed, speciation of forms of iron and manganese in water treatment, and the effects of colloidal iron and manganese on RO operation. The overall conclusion is that methods for the speciation and quantitation of colloidal forms of iron and manganese need to be fully developed and employed for the validation of methods useful for the control and/or removal of such foulants in RO feedwaters.

Keywords: Colloidal iron; Colloidal manganese; Speciation; Quantitation; Reverse osmosis; Membrane fouling; Natural sources; Introduction in pretreatment

1. Background

In the course of solving membrane fouling problems in RO plants, the finding of various forms of iron, and less commonly of manganese, in numerous reverse osmosis (RO) membrane autopsies [1–3], have led us to call attention to the diverse forms of iron and manganese species in natural and treated waters. Correlation of elemental composition analyses of foulants with contaminants in RO feedwater and pretreatment steps led to successful solutions of fouling problems by modification of pretreatments, such as substitution of oxidation filtration strategies for iron and manganese reduction with sequestration with appropriate antiscalants [4,5]. In cases where iron and manganese fouling failed to respond to sequestration with antiscalants, the existence in the RO feedwater of pre-existing colloidal iron and manganese particles are suspected [5,6].

Low levels of iron and manganese in water are not always targets for removal in water purification. In desalination with reverse osmosis (RO) however, they can significantly affect the operation and maintenance of the membranes. Methods of dealing with iron and manganese fouling in RO pretreatment become major issues, especially where maximum recovery of water is needed in areas of the world where water is scarce, or where the disposal of RO concentrate as a waste stream is costly, or not possible [6].

Colloidal particles by definition are particles less than 0.1 micron (100 nanometers) in size. Extremely high surface areas per unit weight lead to novel physical properties of self-assembly, aggregations, patterning of depositions on surfaces that is the core of the rapid development of nanotechnology in this decade [7]. General colloidal fouling of high and low pressure membranes have been briefly reviewed in the past, in connection with humic matter, elemental sulfur and silicates [8] and calcium phosphate [9]. The cake-layer and pore fouling of UF [10] and cake layer fouling of RO [11] by colloidal iron oxide have been studied.

To fully control such colloidal fouling, speciation and quantitation of the different forms iron and manganese that exist in natural, industrial and wastewaters are central to process design, troubleshooting and optimizing RO system operation and maintenance. We have undertaken a literature review of iron and manganese colloidal chemistry as it pertains to the RO membrane process.

2. The linkage of iron and manganese in water treatment

Iron and manganese are chemically similar in oxidation and reduction properties in nature and in treatment processes. In natural waters, solubilization and deposition of iron and manganese compounds are largely regulated by microorganisms as energy sources, as oxidizable fuel in aerobic environments and sources of oxygen in anaerobic environments [12–17]. In water supplies, they cause taste, odor, color, corrosivity, foaming and staining problems. Iron oxyhydroxides give reddish brown color and stains, and manganese oxyhydroxides are brownish black in color and lead to even more noticeable stains. For these aesthetic issues, the Environmental Protection Agency (EPA) in the United States as well as the World Health Organization (18) have set for drinking water standard, Secondary Maximum Contamination Levels (SMCL) of 0.3 mg/l for iron and 0.05 mg/l for manganese. Iron and manganese in natural waters are considered trace nutrients, and do not pose health hazards. For health considerations, the same concentration limits have been set by the US Food and Drug Administration in the quality standard for bottled water.

3. Sources of iron and manganese in water

Iron is a major metallic element in the crust of the earth, estimated to constitute 4–5% of the mass. It is present mainly in the forms of highly water insoluble oxides, principally hematite (Fe_2O_3) and goethite (FeOOH) and innumerable forms of complex silicates. Manganese oxyhydroxide and silicate ores are poorly understood and are amorphous mixtures of manganese in the 2+, 3+ and 4+ oxidation states. Pyrolusite (mainly MnO_2), braunite (manganese silicate) and psilomelane (a complex barium manganese oxyhydroxide) are the main manganese ores. Soils contain about 0.1% Mn oxyhydroxides [19].

Although low concentrations are found in every natural water supply, iron is seldom found at concentrations greater than 10 mg/l and manganese concentrations are typically less than 1 mg/l [20]. The main process by which these minerals dissolve in water appears to be through the energy-generating metabolic actions of microbes which live on reducing iron and manganese in their insoluble higher oxidations states to the more soluble lower oxidation state forms. For instance, ferric oxides and manganese (III-IV) oxides are water-insoluble, while ferrous and manganous salts formed are relatively soluble. Microorganisms such as iron bacteria, can in aerobic environments, oxidize the reduced forms of iron and manganese, including metallic iron and manganese, to the higher oxidation forms.

Once released into water as soluble salts, the ionic forms of iron and manganese can again precipitate as insoluble salts in combination with other anions. For instance, arsenate, boride, chromite, oxyhydroxide, phosphate, silicate and sulfides of iron and manganese are generally insoluble. The precipitated salts can remain suspended and mobile in the water as colloids or can be adsorbed on soil particles or coagulated and flocculated to become larger particles to be removed from the water by filtration.

Corrosion of metal pipes and equipment in municipal water systems aided by iron and manganese bacteria can be a source of iron and manganese release into the water.

4. Forms of iron and manganese in water that affect RO performance

4.1. Ionic iron

Iron in the ionic ferrous form are often seen ranging from 0.5–8.0 mg/l in deep well waters. On exposure to air above ground, it spontaneously oxidize to the ferric form and precipitates as ferric hydroxide. With atmospheric partial pressure of oxygen and pH >6, the chemical half-life of ferrous ion is on the order of minutes to hours [21]. Development of turbidity in the initially clear water is sometimes seen in samples of well water when the oxidized iron begins to coagulate with colloidal organic and inorganic matter such as microbial slime and silica respectively. Iron is the third most common cation in total soil content, amounting to 10–300 g per 1 kg of soil. Of this, only tiny fractions are exchangeable on soil particle surfaces or dissolved in the soil solutions [19].

Ionic iron is commonly added to water as a coagulant in clarification process. High solubilities of synthetic ferrous and ferric chlorides and ferric sulfate allows for the preparation of iron solutions for injection into turbid waters as coagulants prior to sedimentation and filtration. The particles formed by coagulation and subsequent flocculation exist in a wide range of particle sizes which may not be completely removed by adsorption and physical retentions by multimedia and cartridge filters, or even by micro or ultrafiltration (MF/UF) membranes. Colloidal fouling of RO by MF or UF filtrates with Silt Density Index of less than 2 are often seen in seawater and municipal wastewater RO plants.

4.2. Ferric oxyhydroxides and oxides

Hematite (Fe_2O_3) and goethite (FeOOH) are the most common iron oxides found in soils [19]. Hematite is pink to bright red. Goethite is brown to dark yellowish-brown. Both hematite and goethite occur as amorphous coatings on soil particles, impacting the red and brown colors characteristic of soils. Their content can be 20–30% of the soil in highly weathered regions. Magnetite (Fe_3O_4) is a magnetic iron oxide inherited from parent rock. It usually occurs as sand-sized grains of high specific gravity. The precipitation of amorphous iron hydroxides is responsible for the irreversible hardening upon drying of soils into stone-like materials.

Iron oxyhydroxide and oxides are highly insoluble in water. They are solubilized as ferrous salts in ground waters by microbial actions, and can subsequently reprecipitate as oxyhydroxides on exposure to air or again by microbial action. A large class of iron bacteria has been characterized [12,22,23]. These same bacteria are involved in the corrosion of iron and steel in water treatment equipment and water distribution systems, returning them to the natural oxyhydroxide and oxide states.

In seawater, ferric iron concentration has been reported to range from 0.02 to 0.27 mg/l [24]. Iron is considered perhaps the most important of all bioactive trace elements. However, its marine chemistry and inorganic speciation are rather complex and still not adequately understood [25]. In the photic zone of the ocean surface, a continuous reduction then oxidation cycling of Fe(II)–Fe(III) occurs as a photochemical process, forming a colloidal ferric hydroxide that is less polymeric and less crystalline than aged ferric hydroxide. This form is more soluble and in faster equilibrium with monomeric ferric species which may control iron uptake by phytoplankton. A similar photochemical cycling process most likely occurs for manganese as well.

4.3. Colloidal silicates containing iron and manganese

Elemental composition of the crust of the earth is dominated by oxygen and silicon atoms, with aluminum, calcium, magnesium, and iron as the main metal elements and manganese as a minor component incorporated in a wide variety of combinations as mixed silicates [26]. Iron is widely incorporated in silicate minerals such as biotite, olivine, chrysotiles and magillite. Erosion of such minerals by water would generate iron-containing silicates in the colloidal size range that affect RO membranes.

The facile polymerization reaction of ionic iron in water with reactive silica added as sodium silicate [1,27] points to the mechanism by which colloidal iron and manganese silicates can form in waters containing soluble iron, manganese and reactive silica, and by themselves or become a part of complex coagulate with organic colloids that foul membranes.

The weathering and microbial process reducing mineral particle sizes smaller and smaller and the chemical precipitation and microbial particle growth process represents the “top down” and the “bottom up” routes respectively by which particles in the colloidal range are formed.

4.4. Colloidal organic matter containing iron and manganese

Positively charged trivalent ferric ion is an effective coagulant towards organic and inorganic colloids in natural waters. Ferric chloride and ferric sulfate are widely used as coagulant in the clarification of surface and seawater as pretreatments to RO. Due to the prevalence of exocellular polysaccharides, humic plant matter, bacteria, planktons and other microorganisms in these waters, and often incomplete coagulation/flocculation before multimedia and cartridge filters, colloidal organic matter containing iron are often found among the RO membrane foulants.

In brackish waters from wells containing iron and manganese, a number of different species of iron bacteria can be found [12,22,23]. They derive energy by oxidizing dissolved iron and manganese in the reduced forms into the insoluble oxidized forms, causing precipitation and accumulation of black or reddish brown gelatinous slime. Minute dispersions of these particles can be expected to mobilize in water as iron-containing organic colloids. Studies consistently show that colloids as well as organic and inorganic complexes are important for all heavy metals in landfill leachates [28].

4.5. Colloidal goethite and hematite

Iron oxyhydroxides have net positive charges in acid soils due to hydrogen ion adsorption. As the pH of the ground water increases, the charge changes from positive to negative as hydrogen ions dissociate [19]. This might contribute to the mobilization of colloidal goethite and hematite in ground water [29,30]. Such iron-rich colloids play prominent roles in subsurface transport by water of contaminants which are of great concern for the containment of buried wastes [31–34].

4.6. Colloidal iron and manganese formed in oxidation/coagulation/filtration treatments

Oxidation of dissolved ferrous and manganous salts followed by coagulation and filtration often, if not invariably, allows a carryover of some amounts of colloidal iron and manganese foulants affecting the operation of downstream RO systems. Iron is usually oxidized catalytically by air or with manganese greensand fed continuously with chlorine or potassium permanganate as oxidants. Manganese is more difficult to oxidize requiring catalyzed chlorine, ozone, chlorine dioxide, or potassium permanganate [35–41]. It should be noted that black manganese dioxide dust is the main form of oxidized manganese being formed from the oxidation of the dissolved manganese species and shed from the manganese greensand bed as well as being the product of the reduction of potassium permanganate.

Iron and manganese in drinking water can be considered as being present in three physical forms: 0.45 micron filter removable particles, colloidal particles that pass 0.45 micron filters and dissolved ions. For drinking water compliance testing, samples filtered with 0.45 micron filters are analyzed by emission spectroscopy for total iron or manganese. Such results would include both colloidal and ionic forms of the metals. Iron and manganese removal efficiencies in municipal water plants vary with the reagents used, initial iron and manganese concentrations, pH and ionic strength [38,42]. The oxyhydroxide particles are formed with a range of particle sizes that are partially removed by the standard coagulation, flocculation and filtration methods employed [38,40,42,44]. Laboratory studies showed that removal of particles in the colloidal range posed a significant challenge [35,37–39,41]. In natural waters, oxidative removal of iron and manganese is further complicated by their complexation with natural organic matters [45–47].

5. Speciation of iron and manganese

In water samples, iron and manganese may occur in true solution in ionic form, paired with anions and complexing molecules that allow it to remain in solution. As larger molecular aggregates, they may occur as colloidal complexes in the size range of 0.1 to 0.001 microns. They remaining in solution as particles invisible to the naked eyes, and not removed by filtration through 0.45 micron filters, which are ususlly used in analytical laboratories to define “soluble” analytes. Larger particles in the particle-size continuum begin to be retained by 0.45 micron filters, and contribute to Silt Density Index and turbidity values of importance to RO system control.

In water, ferrous and ferric ions are differentiated and measured by colorimetric assays. Highly colored complexes with thiocyanate, 1,10-phenanthroline and thioglycollic acid can differentiate between Fe(II) and Fe(III) ions. Under reducing conditions, iron exists in the Fe(II) state. On exposure to air or the addition of oxidants, Fe(II) is readily oxidized to Fe(III) state and may hydrolyze to form insoluble ferric hydroxide. In the absence of solubilizing complexing agents, ferric hydroxide precipitates unless the pH is kept very low.

Fe(III) reacts with thiocyanate (SCN^-) ions to give a series of intensely red-colored compounds, which remain in true solution; Fe(II) does not react. In the colorimetric assay, a large excess of thiocyanate is used to increase the intensity and stability of the color. Hydrochloric or nitric acid at 0.05–0.50 M concentrations are used to suppress the precipitation of ferric hydroxide.

Fe(II) reacts with 1,10-phenanthroline to form an orange-red complex. The color intensity is independent of the acidity in the pH range 2–9, and is stable for long periods. By this method, both Fe(II) and Fe(III) can be determined spectrophotometrically: the reddish-orange Fe(II) complex absorbs at 515 nm, and both the Fe(II) and the yellow Fe(III) complex have identical absorption at 396 nm, the amount being additive. The solution, slightly acid with sulfuric acid, is treated with 1,10-phenanthroline, buffered with potassium hydrogen phthalate at a pH of 3.9: the reading at 396 nm gives the total iron and that at 515 nm the Fe(II).

The use of thioglycollic acid (mercaptoacetic acid) for the determination of iron is of importance because it is relatively free from interferences giving a red-purple color with Fe(III) which can be measured at 535 nm.

A US Army Corp of Engineers report [48] described using a,a’-dipyridyl and ferrozine as color reagents for ferrous ion, measuring absorbances at 520 nm and 526 nm respectively. Addition of hydroxylamine hydrochloride to the samples reduced the ferric ions in the same samples to ferrous ions. Repeat of the colorimetric assay for ferrous ions then provided a measurement of the total iron, and ferric ions by the difference. Manganese was analyzed using formaldoxine colorimetric reagent which quantitated the Mn^{2+} ion [49].

Speciation of iron and manganese particles by fractionation by size with filters of a range of pore-sizes have been reported [38,41]. The scheme of two filtration steps were used in fractionation [38]: 0.2 micron filter removed particulate metal species, followed by passage through an ultrafilter with 30,000 molecular weight cutoff (MWCO) to separate colloidal particles from the dissolved species. Emission spectroscopic standard methods by atomic absorption or inductively coupled plasma provide total iron and manganese assays without differentiating the metal oxidation states, whether complexed, or as soluble, colloidal or particulate forms. By the two step filtration scheme, the reductions in total metal content can be attributable to particulate and colloidal fractions. For the fractionation of manganese particles, ultrafilters of 3, 10, 30 and 100 K MWCO were compared [38,41]. The 3, 10 and 30K MWCF membranes retained about the same amount of Mn and significantly more than the 100 K membrane [38].

More recently, sequential laser pulses have been used to amplify particulate forms by breaking apart iron-containing particles into smaller fragments [50]. A paper on quantitative determination of the elemental, ferrous, ferric, soluble and complexed iron in foods [51] has been widely referred to in subsequent studies by others on speciation of iron in foods.

6. Effects of iron and manganese species on RO operation

Presence of iron in RO foulants, often in significant amounts, is commonly seen in elemental composition analyses performed in conjunction with membrane autopsies for the resolution of fouling problems [1–3]. Iron-containing colloidal oxides, silicates, sulfides and phosphates in RO feedwaters often contribute to the elemental compositions of foulants obtained from membrane surfaces. In cases where well waters have high iron content, and pretreatment steps such as manganese greensand or other oxidation/filtration are used to reduce iron concentration in RO feedwaters, ferric hydroxide and iron-coagulated pretreatment chemicals usually are found on the membranes as foulants [5].

Citing some examples in the United States, colloidal iron and silica in well water is the limiting factor in RO water recovery in the Eastern Municipal District desalters in southern California, and is the subject of a laboratory study [52]. Morro Bay seawater RO required iron removal pretreatment due to severe precipitation of iron in well water requiring changing of cartridge filters every half hour [53]. Alluvial and San Diego Formation wells supplying Sweetwater desalter in San Diego contained iron and manganese particles led to a study of the oxidation and removal of iron and manganese by the pretreatment combination of aeration and low-pressure membrane filtration to improve RO performance [54]. Pretreatment for the removal of iron and manganese posed a major design challenge for the 8–24 mgd RO plant in the City of Abilene, Texas [55].

We have for some years advocated the use of antiscalants to sequester iron and manganese so that contaminated ground water can be fed directly to RO systems without pretreatment [4]. This strategy has worked extremely well. In Saskatchewan, Canada and in many regions of central United States, well waters with up to 8 mg/l of iron are routinely injected with just an antiscalant, kept from exposure to air where possible, and sent directly to the ROs through just the cartridge filter [5]. In contrast, existing RO plants using the traditional oxidative filtration iron/manganese removal pretreatments often suffer severe fouling problems due to incomplete removal of iron, or colloidal iron/manganese particles actually generated by such pretreatment steps. Using an appropriate antiscalant to control all scaling potentials of the RO feedwater as well as the sequestration of iron and manganese allows for the elimination of existing pretreatments like manganese greensand filters and multimedia filtrations following oxidation of iron. When this change is made, invariably fouling problems ceased.

It is well to keep in mind that when well waters contain 1 mg/l or more of ferrous iron, air oxidation will generate in the water an excellent coagulant to coagulate with bacterial slime, colloidal clays, silica and organic matter [1]. It is widely observed that well waters containing iron can turn visibly turbid within one hour of exposure to air. Such RO feedwaters have led to RO membrane foulants composed of organics, silicates and iron. Even without colloidal mass present in the water to coagulate with ferric iron, some ferric hydroxide precipitate itself can remain in colloidal form, and escape filtration by multimedia and cartridge filters. Colloidal particles coagulate within the RO when salinity rises. Colloidal iron being positively charged particles, adsorb on the membrane surfaces, and on the layer of foulants already deposited on the membrane surface.

The use of manganese dioxide-coated greensand as iron removal filter deserves a special mention as a source of RO membrane fouling. Colloidal particles of manganese dioxide whether shed from the manganese greensand or carried over from the reduction of potassium permanganate used in the regeneration of manganese greensand are found to be present to varying degrees as brownish black coatings on RO membranes. In cases where manganese dioxide coating is not maintained on the greensand by consistent maintenance with potassium permanganate or other oxidizing agents to sustain the filter-bed as iron-oxidizing and removal tower, we have found colloidal greensand coatings on the membranes. Greensand (glauconite) has the signature elemental composition of $K_2(Mg,Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}$. Being a zeolite with the crystal lattice positions occupied by the ion-exchangeable potassium and magnesium atoms, the greensand appears to be brittle as a packing material in multimedia filters. Over periods of use, small expansions and contractions resulting from cation exchange activities appears to cause the sloughing off of colloidal fragments of the greensand that are small enough to pass the micron cartridge filters and enter the membrane elements as colloidal foulants.

The effects of membrane fouling by all colloidal iron and manganese species begins with flux reduction from a thin coating, to differential pressure rise from heavier depositions. Any carryover of traces of oxidants like hypochlorite and chloramine in the feedwater catalyzed by iron and manganese as foulants on the membrane will cause severe loss of salt rejection due to free-radical reactions damaging the polyamide barrier layer of the thin-film composite membrane.

7. Conclusions

A large variety of iron and manganese-containing species exist in RO feedwaters. Due to the high valence states and positive charges of iron and manganese ions, even low concentrations of these ions act as coagulants in RO feedwaters. The resulting colloidal particles containing iron and manganese that are formed in natural waters can contain positive surface charges, causing them to be attracted to the negative charges on the membrane surfaces, and to the generally negatively charged surfaces of natural microbial and humic colloids. Once attached to the membranes, iron and manganese-containing foulants cause a progression of flux reduction, differential pressure rise, and increase in salt passage by membrane polarization effect or more severely by membrane oxidative damage in the presence of oxidants.

To control such negative effects of iron and manganese species in water affecting RO operation, a successful approach in recent years in process design and conversion of problematic existing pretratment processes is to eliminate iron oxidation and removal steps. Instead, antiscalants are used for iron and manganese sequestration (4) keeping iron and manganese in solution without aggravating a colloidal fouling tendency that already exists in some waters.

References

[1] R.Y. Ning and D. Stith, The iron, silica and organic polymer triangle. Ultrapure Water, 14(3) (1997) 30–32.

[2] R.Y. Ning and P.T.L. Shen, Observations from analysis of reverse osmosis membrane foulants. Ultrapure Water, 15(4) (1998) 37–40.

[3] E.G. Darton, and M. Fazel, A statistical review of 150 membrane autopsies. Proc. Intern. Water Conf., Pittsburgh, PA, Paper IWC-01-23, 2001, pp. 157–163.

[4] R.Y. Ning, Process simplification through the use of antiscalants and antifoulants. Ultrapure Water, 20(7) (2003) 17–20.

[5] R.Y. Ning, T.L. Troyer and R.S. Tominello, Antiscalants for near complete recovery of water with tandem RO process, Desal. Wat. Treat, 9 (2009) 92–95.

[6] R.Y. Ning and T.L. Troyer, Tandem reverse osmosis process for zero-liquid discharge. Desalination, 237 (2009) 238–242.

[7] G.A. Ozin and A.C.Arsenault, Nanochemistry — A Chemical Approach to Nanomaterials, Royal Society of Chemistry, Cambridge, UK, 2005.

[8] R.Y. Ning, T.L. Troyer and R.S. Tominello, Chemical control of colloidal fouling of reverse osmosis systems. Desalination, 172 (2005) 1–6.

[9] R.Y. Ning and T.L. Troyer, Colloidal fouling of RO membranes following MF/UF in the reclamation of municipal wastewater. Desalination, 208 (2007) 232–237.

[10] Y. Soffer, J. Gilron and A. Adin, Streaming potential and SEM–EDX study of UF membranes fouled by colloidal iron. Desalination, 146 (2002) 115–121.

[11] S.G. Yiantsiois and A.J. Karabelas, An assessment of the Silt Density Index based on RO membrane colloidal fouling experiments with iron oxide particles. Desalination, 151 (2002) 229–238.

[12] D.R. Cullimore and A.E. McCann, The identification, cultivation and control of iron bacteria in ground water, in F.A. Skinner and J.M. Shewan, eds., Aquatic Microbiology. Academic Press, New York, NY, 1977.

[13] R.L. Starkey, Transformation of iron by bacteria in water, J. AWWA, 37 (1945) 963.

[14] W.C. Ghiorse, Biology of iron and manganese depositing bacteria. Annu. Rev. Microbiol., 38 (1984) 515.

[15] R.S. Wolfe, Microbial concentration of iron and manganese in water with low concentrations of these elements, J. AWWA, 52 (1960) 1335.

[16] S.D. Chapnick, W.S. Moore and K.H. Nealson, Microbially mediated manganese oxidation in a fresh water lake. Limnology Oceanography, 27 (1982) 1004–1014.

[17] K.H. Nealson, B.M. Tebo and R.A. Rosson, Occurrence and mechanisms of microbial oxidation of manganese. Adv. Appl. Microbiol., 33 (1988) 299–318.

[18] J. Amman, Guidelines for Drinking Water Quality, Vol. 1, WHO, 1995.

[19] H.L. Bohn, B.L. McNeal and G.A. O'Connor, Soil Chemistry, 3rd ed., John Wiley, New York, NY, 2001.

[20] D. Gregory and K. Carlson, Effect of soluble Mn concentration on oxidation kinetics. J AWWA, 95(1) (2003) 98–108.

[21] W. Sung and E.J. Forbes, Some considerations on iron removal. J. Environ. Eng., 110(6) (1984) 1048.

[22] F.M. Clark, R.M. Scott and E. Bone, Heterotrophic iron-precipitating bacteria. J. AWWA, 59(8) (1967) 1036.

[23] R.S. Wolfe, Cultivation, morphology, and classification of the iron bacteria. J. AWWA, 50 (1958) 1241.

[24] S. El-Manharawy and A. Hafez, Could seawater be under saturation and acidic? Desalination, 165 (2004) 43–69.

[25] W. Stumm and J.J. Morgan, Aquatic Chemistry, 3rd ed., John Wiley, New York, NY, 1996, pp. 646–649.

[26] F. Liebau, Structural Chemistry of Silicates. Springer–Verlag, New York, NY, 1985.

[27] F.J. Dart and P.D. Foley, Preventing iron deposition with sodium silicate. J. AWWA, 62(10) (1970) 663.

[28] D.L. Baun and T.H. Christensen, Speciation of heavy metals in landfill leachate: a review. Waste Manage. Res., 22(1) (2004) 3–23.

[29] D. Langmuir, Geol. Surv. Prof. Pap. US, 650-C (1969) C224.

[30] A. Wolthoorn, E.J. Temminghoff and W.H. van Riemsdijk, Effect of synthetic iron colloids on the microbiological NH_4^+ removal process during ground water purification. Water Res., 38(7) (2004) 1884–1892.

[31] J.F. McCarthy and J.M. Zachara, Subsurface transport of contaminants. Environ. Sci. Technol., 23(5) (1989) 496.

[32] J.F. McCarthy and L.D. McKay, Colloid transport in the subsurface: past, present, and future challenges. Vadose Zone J., 3 (2004) 326.

[33] J.F. Ranville, D.J. Chittleborough and R. Beckett, Particle-size and element distributions of soil colloids: Implications for colloid transport. Soil Sci. Soc. Am. J., 69 (2005) 1173.

[34] T. Kanti Sen and K.C. Khilar, Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. Adv. Colloid Interface Sci., 119(2–3) (2006) 71–96.

[35] W.R. Knocke, J.E. Van Benschoten, M.J. Kearney, A.W. Soborski and D.A. Reckhow, Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide. J. AWWA, 83(6) (1991) 80–87.

[36] J.E. Van Benschoten and W. Lin, Kinetic modeling of manganese(II) oxidation by chlorine dioxide and potassium permanganate. Environ. Sci. Technol., 26 (1992) 1327–1333.

[37] A. Wilczak, W.R. Knocke, R.E. Hubel and E.M. Aieta, Manganese control during ozonation of water containing organic compounds. J. AWWA, 85(10) (1993) 98–104.

[38] K.H. Carlson, W.R. Knocke and K.R. Gertig, Optimizing treatment through Fe and Mn fractionation. J. AWWA, 69(4) (1997) 162–171.

[39] D. Gregory and K. Carlson, Effect of soluble Mn concentration on oxidation kinetics. J. AWWA, 95(1) (2003) 98–108.

[40] A. Maleki, B. Roshani and F. Karakani, Study on the efficiency of the different units for removing metallic ions in Isfahan water

treatment plant. J. Appl. Sci. Environ. Manage., 9(2) (2005) 61–64.
[41] J. Sallanko, E. Lakso and M. Lehmikangas, The effect of ozonation on the size fractions of manganese. Ozone: Sci. Eng., 27(2) (2005) 147–152.
[42] L. Liang and J.J. Morgan, Chemical aspects of iron oxide coagulation in water: laboratory studies and implications for natural systems. Aquatic Sci., 52(1) (1990) 1615–1621.
[43] L.D. Benefield and J.F. Judkins, Iron and manganese removal, in Process Chemistry for Water and Wastewater Treatment, Prentice-Hall, New York, NY, 1982.
[44] J.M. Montgomery, Water Treatment Principles and Design. John Wiley, New York, NY, 1985.
[45] P. Bene and E. Steinnes, In situ dialysis for the determination of the state of trace elements in natural waters. Water Res., 8 (1974) 947–953.
[46] M.D. Krom, On the dissociation of iron and manganese with organic matter in anoxic marine pore waters. Geochim. Cosmochim. Acta, 42 (1978) 607–611.
[47] H. Borg, in L. Landner, ed., Fractionation of Metals in Water, Sediment, and Soil Systems. Springer–Verlag, Berlin, 1987.
[48] S.P. Faulkner, R.P. Gambrell and S.L. Ashby, Analytical methods for iron and manganese determinations in reservoir tailwaters: laboratory investigations. US Army Corps of Engineers, Water Quality Technical Note PD-01, January 1996.
[49] J.J. Morgan and W. Stumm, Analytical chemistry of aqueous manganese. J. AWWA, 58 (1965) 107–119.
[50] S. Nakamura, Y. Ito and K. Sone, Determination of an iron suspension in water by laser-induced breakdown spectroscopy with two sequential laser pulses. Anal. Chem., 68(17) (1996) 2981.
[51] K. Lee and F.M. Clydesdale, Quantitative determination of the elemental, ferrous, ferric, soluble and complexed iron in foods. J. Food Sci., 44(2) (1979) 549.
[52] A. Zacheis, A bench-scale approach to optimize of reverse osmosis systems treating silica and iron bearing groundwater. AWWA Inorganic Contaminants Workshop, Austin, TX, 2006.
[53] E. Kartinen, Jr. and C. Martin, Solving Morro Bay's seawater reverse osmosis plant's iron problem. Membrane Technology Conf. Proc., AWWA, Atlanta, GA, March 2–5, 2003.
[54] M.A. Mann, D.Thomson, E. Jabari and D. Rohe, Microfiltration and ultrafiltration: novel pretreatments for iron and manganese removal from a reverse osmosis feedwater. Water Quality Technology Conf. AWWA, Seattle, WA, November 10–14, 2002.
[55] B. Yallaly, R.Bergman, B.Fuerst and R. Foster, Process selection and design of a dual-membrane treatment plant treating brackish surface water. Annual Conf. Proc., AWWA, Washington, DC, June 17–21, 2001.