Finding Balance between Biological Groundwater Treatment and Treated Injection Water – 15237

Mark Carlson *, Eli Ludwig **, Sally Simmons *, Ken Martins ***, James Geiger *, Kellin Nielsen *, Louis Watkins *, Phillip McFee *, John Morse ****, Mark Byrnes *
* CH2M HILL Plateau Remediation Company
** Groundwater Partners, Inc.
*** CH2M HILL
**** US DOE

ABSTRACT

At the U.S. Department of Energy's Hanford Site, CH2M HILL Plateau Remediation Company operates the 200 West Pump and Treat which was engineered to treat radiological and chemical contaminants in groundwater as a result of the site's former plutonium production years. Fluidized bed bioreactors (FBRs) are used to remove nitrate, metals, and volatile organic compounds. Increasing nitrate concentrations in the treatment plant effluent and the presence of a slimy biomass (a typical microorganism response to stress) in the FBRs triggered an investigation of nutrient levels in the system. Little, if any, micronutrient feed was coming into the bioreactors. Additionally, carbon substrate (used to promote biological growth) was passing through to the injection wells, causing biological fouling of the wells and reduced specific injectivity. Adjustments to the micronutrient feed improved microorganism health, but the micronutrients were being overfed (particularly manganese) plugging the injection wells further. Injection well rehabilitation to restore specific injectivity required repeated treatments to remove the biological fouling and precipitated metal oxides. A combination of sulfamic and citric acids worked well to dissolve metal oxides and sodium hypochlorite effectively removed the biological growth. Intensive surging and development techniques successfully removed clogging material from the injection wells. Ultimately, the investigation and nutrient adjustments took months to restore proper balance to the microbial system and over a year to stabilize injection well capacities. Carefully tracking and managing the FBRs and well performance monitoring are critical to balancing the needs of the treatment system while reducing fouling mechanisms in the injection wells.

INTRODUCTION

The 200 West Pump and Treat (P&T), located on the U.S. Department of Energy's Hanford Site, is designed to capture and treat contaminated groundwater to reduce the mass of carbon tetrachloride, total chromium (trivalent and hexavalent), nitrate, trichloroethene, iodine-129, and technetium-99 throughout the 200-ZP-1 Operable Unit. The facility can treat up to 9,464 L/min (2,500 gallons per minute [gpm]) of extracted groundwater using two parallel treatment trains. The effectiveness of the remedy is further enhanced by controlling the direction and rate of groundwater flow throughout the 200-ZP-1 Operable Unit using strategically-placed extraction and injection wells for flow-path control.

The groundwater treatment approach involves multiple treatment steps to remove contaminants. Groundwater from wells containing radioactive contaminants is pumped through an ion exchange system, which removes technetium-99 and iodine-129 using a Purolite A530E[1] resin, then on to an equalization

[1] Purolite is a registered trademark of BROTECH CORP., Bala Cynwyd, Pennsylvania.

tank where it is blended with groundwater from wells without radioactive contaminants. The water passes through a recycle tank and up through the fluidized bed bioreactors (FBRs). MicroCg™ (i.e., organic carbon substrate used as the electron donor in biological denitrification), phosphoric acid, and a micronutrient solution are fed immediately upstream of the FBRs to facilitate biological denitrification. These three chemicals provide food and nutrients for a denitrifying biofilm that is grown on granular activated carbon in the FBRs. The treated FBR effluent is discharged into carbon separators before the denitrified groundwater flows into a splitter structure to divide the stream amongst four membrane bioreactors (MBRs) for removal of solids by membrane filtration, residual carbon substrate by aerobic biodegradation, and carbon tetrachloride, chloroform, and trichloroethene by air stripping. Off-gas from the air stripper, influent equalization tank, strip tanks, FBRs, membrane tanks, sludge holding tanks, rotary drum thickeners, and centrifuges is combined and treated by Vapor Phase Granular Activated Carbon (VPGAC). To avoid buildup of radionuclides in the VPGAC, air streams to the VPGAC system are pre-treated by a demister to minimize liquid carryover.

The treated effluent is then conveyed through a series of pipelines and injected into the aquifer via the injection well field. Injection wells are installed both upgradient (to direct the contaminant flow toward the extraction wells) and downgradient (to slow contaminant flow toward the Columbia River).

Problem

The first indications of a problem with the 200 West P&T were increasing nitrate concentrations in the effluent in spring of 2013. Additionally, the presence of excessive amounts of a slimy biomass in the FBRs triggered an investigation to find the cause. The microorganisms in flocculated biological systems such as biofilms reside in a complex matrix of proteins, lipids, polysaccharides, nucleic acids, and humic substances called extracellular polymeric substance (EPS). Stresses impacting the microorganisms, such as nutrient limitations, can cause an overproduction of EPS. The overproduction of EPS appears as a slimy biomass. A sampling campaign provided strong evidence that micronutrient limitation was the cause of EPS overproduction that led to the FBR upsets and the increasing nitrate concentrations in the effluent [1].

FBR Problems

Pacific Northwest National Laboratory performed a preliminary qualitative screening to determine the presence or absence of denitrifying and other bacteria. The results indicated denitrifying bacteria were present, but represented only about 10 percent of the population. Sulfate- and iron-reducing bacteria accounted for only a small percentage. It was surmised that aerobic heterotrophic bacteria dominated the FBR microbial population. In a system where denitrification is the desired reaction, and oxygen needs to be depleted at the surface of the biofilm before denitrification can occur, the available micronutrients may have become depleted making one or more micronutrients the limiting substrate for denitrification. Many micronutrients were identified as being fed at rates insufficient to sustain necessary biochemical reactions to support denitrifying bacterial populations. In response, a new micronutrient mixture was created (approximately 10 times the strength of the original solution) and fed at an increased rate to meet micronutrient targets based on a previous denitrifying biofilm system design. Reduced carbon dosing coupled with increased micronutrient dosing increased the relative abundance of denitrifiers to 50 percent during a second sampling event [1].

Injection well performance is naturally related to the treatment plant's effluent water quality. The complexity of the 200 West P&T system's treatment processes (especially related to the FBRs) presumably results in byproducts that are carried in the effluent and, under the right conditions, can lead to injection well fouling and plugging (Fig. 1). Effluent metal and nutrient reduction (especially manganese and iron) will decrease the risk of well fouling and precipitation of solids in the injection well filter pack and formation. Chemical rehabilitation will likely be required multiple times per year per injection well given the current effluent water quality, and damage to the filter pack and formation may be (or become) partially irreversible, meaning the well will never return to the specific capacity/injectivity when it was first installed.

Injection Well Problems

Initially, injection wells lost capacity as a result of biological fouling. As the health of the FBRS declined, unconsumed carbon substrate passed through the FBRs to the treatment plant effluent. During early injection well rehabilitation events, large quantities of biological growth were removed as observed in the video surveys (Fig. 1).

Available analytical results related to the injection well water quality were evaluated. One sample consisted of the solid material collected from an injection well drop pipe. The analytical results indicated that iron and manganese had the greatest concentrations at 49,000 ppb and 27,600 ppb, respectively. These results are consistent with the field observations made during injection well rehabilitation work where the scale or deposits on the injection pipe, sounding tube and conveyance line had similar appearance as manganese dioxide scale or iron oxide scale observed at other project sites. The scale, rather fine grained in nature, is likely self-catalyzing and once established becomes very aggressive (meaning it continues to precipitate and at an increasing rate), resulting in a black slime (when wet) or black powdery coating (once dried). The black material coats the gravel pack and formation sand grains and begins filling the porosity of the gravel pack and formation near the well. As this continues, a halo of decreased permeability develops around the well, resulting in a specific injectivity decline. Typically, the slope of the specific injectivity begins to decrease at an increasing rate for these types of clogging or plugging mechanisms. A chemical rehabilitation will remove the plugging mass that has been deposited around the well resulting in an increase in the injectivity in the short term; however, if the water quality of the treatment plant effluent is unchanged after rehabilitation, the residual manganese dioxides or iron oxides provide the

Fig. 1. Injection well screen before rehabilitation and after one rehabilitation in October 2013. Note the clogging metal oxides remaining on the well screen after rehabilitation.

foundation for future aggressive well plugging in the long term.

Manganese

Manganese is one of several critical micronutrients added to the biological process in the form of a "micronutrient solution." Fig. 2 shows the concentration of manganese in the treatment plant effluent. The effluent manganese concentration peaked in spring of 2013 when the dose was increased to get the biological process under control. Since the summer of 2013, the effluent manganese concentration has systematically declined as the micronutrient solution for the FBRs was slowly and methodically adjusted to maintain microorganism health and to decrease the manganese concentration in the effluent. Manganese has long been known to precipitate in water distribution systems, plate out on and stain plumbing fixtures, and accumulate, corrode, and clog industrial fixtures. Manganese is also a known well-fouling mechanism where manganese occurs naturally or as a byproduct of bioremediation. In other systems operated by CH2M HILL, injection well manganese sensitivity related to well performance has been observed at concentrations as low as 0.01 mg/L manganese in the effluent.

Based on the well performance over time, there is roughly a 3-month lag in the response to improved manganese effluent water quality (Fig. 3). It is expected that the wells will respond rapidly in a loss of

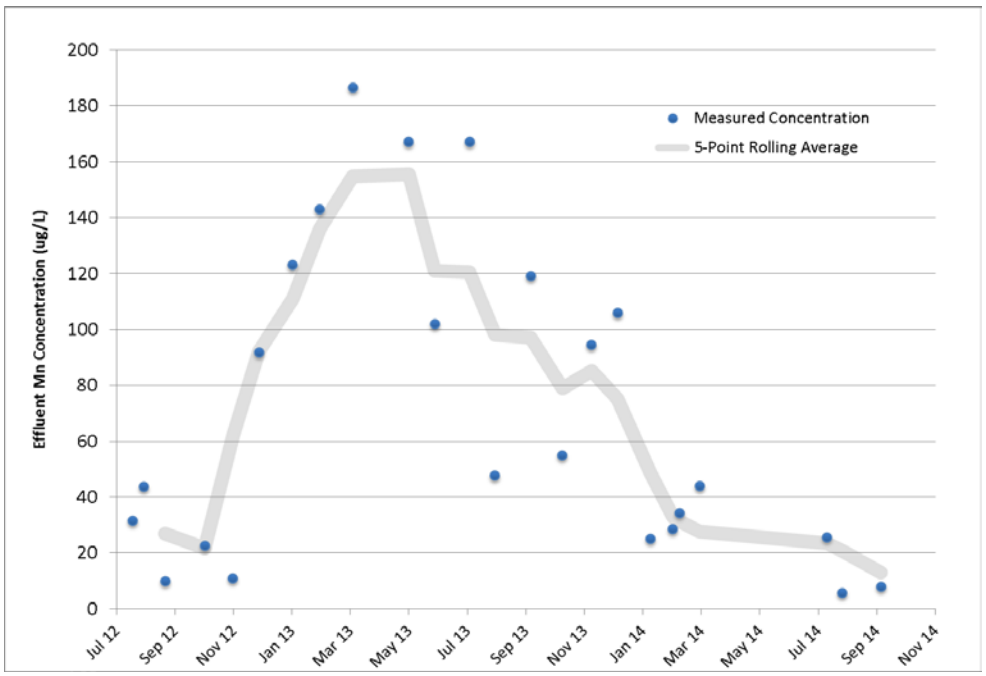

Fig. 2. Manganese concentration in treatment plan effluent

well performance if increases in the effluent manganese concentration occurs, but will then respond slowly (with a gain or stabilization in well performance) when the manganese concentration is corrected and decreased in the effluent (Fig. 3). Note the increase in injection well specific capacity before rehabilitation events.

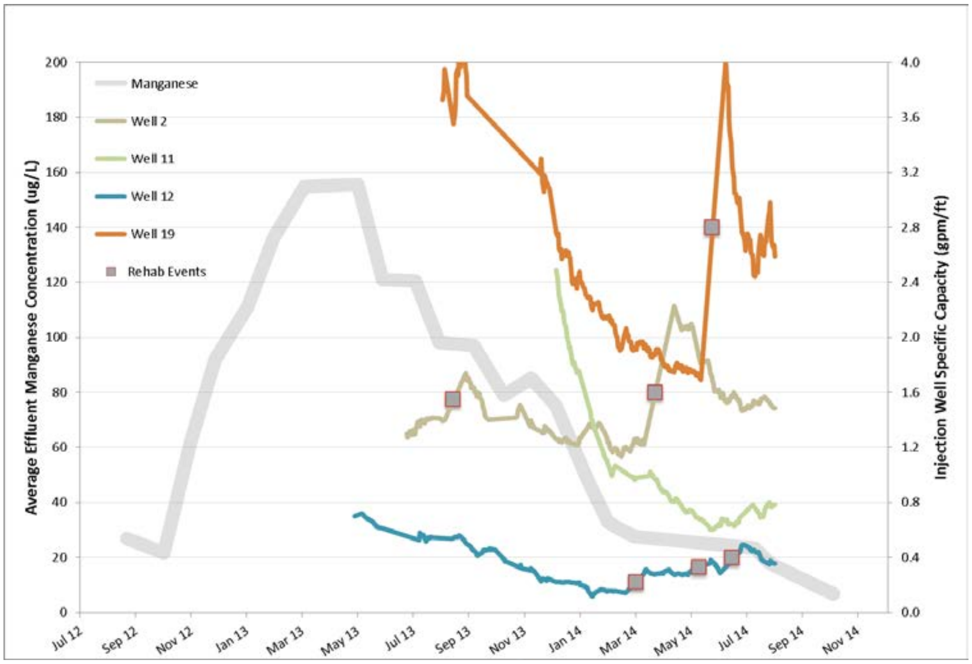

Fig. 3. Improved injection well performance to manganese effluent water quality.

From an injection well standpoint, it is also clear that bacteria and the associated biofilm will clog the injection well as much or perhaps more than the manganese dioxide. Fig. 1 shows the biofilm before and after cleaning. Before cleaning the biofilm occludes the well screen almost entirely. The stringy nature of the biofilm is typical as the EPS is made of polymeric substances. This material is known to clog instrumentation and mechanical equipment at the plant. Note also that the biofilm is readily removed with the exception of a material between the main struts of the well screen. This material is thought to be a corrosion byproduct.

Carbon Substrate

Carbon substrate is added to the biological process as part of the treatment regime. Carbon substrate serves as the energy source or food for bacteria and raw material for the biofilm. The carbon substrate concentration is measured as chemical oxygen demand. This indirect measurement has long been used by sanitary engineers to minimize the amount of oxygen removed from receiving waters. Chemical oxygen demand is related to the organic carbon concentration by the following formula derived from Stumm & Morgan [2]:

$$COD = TOC\left(1 - \frac{oxidation\ state}{4}\right)$$

Where:

TOC = total organic carbon mole O_2/L

COD = chemical oxygen demand in mole C/L

(Eq. 1)

Fig. 4 shows the concentration of COD in the injection water. The concentration peaked at about the same time frame that the manganese concentration peaked.

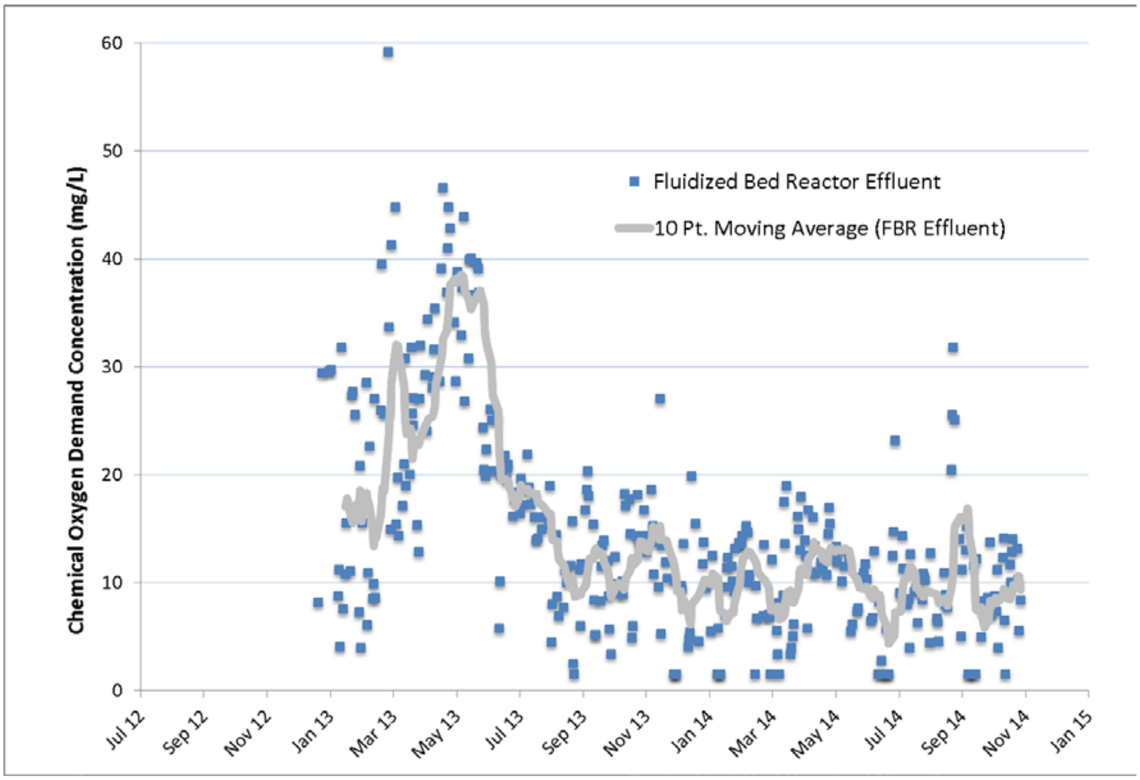

Fig. 4. Chemical Oxygen Demand in water from Fluidized Bed Reactors. Note injection water COD is 2 to 4 mg/L less than that shown.

Nature of the Foulant

Fig. 5 illustrates the black nature of the foulant. Manganese dioxide forms a black precipitate and is thought to be responsible for the color. Fig. 6 shows the material in Fig. 5 magnified 400x. Much of this material shown is thought to be of biological origin. The particles are likely manganese dioxide. The slimy biomass surrounding the precipitated manganese is mainly extracellular polymeric substances with some bacteria.

Fig. 5. Black gelatinous well foulant removed from injection well.

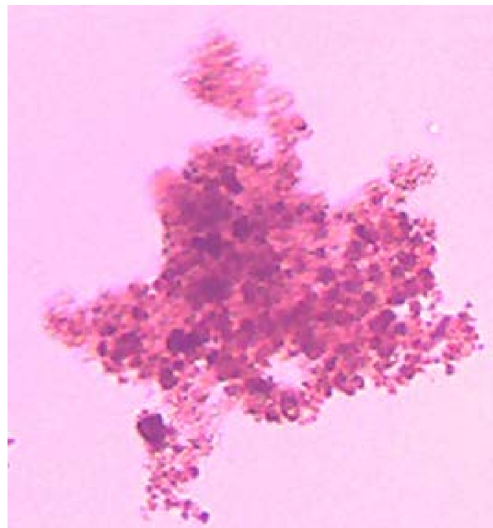

Fig. 6. Gelatinous material in Fig. 4 magnified 400x.

The presence of EPS is necessary for the microbially-mediated oxidation of manganese. EPS is the primary component of most slimy biomass, occupying up to 90% of the volume in the slimy biomass (Fig. 7). The EPS provides an environment where the necessary compounds are trapped in proximity.

Table I lists the results of a chemical analysis of the slimy biomass material. Although much of the material was found to be organic in nature, manganese and iron are present in high concentrations. Both of these metals are added as micronutrients, but their high concentration in the biofilm found on the well screen is a result of bio-magnification. Extracellular polymeric substances act as chelating agents to trap the metals [3].

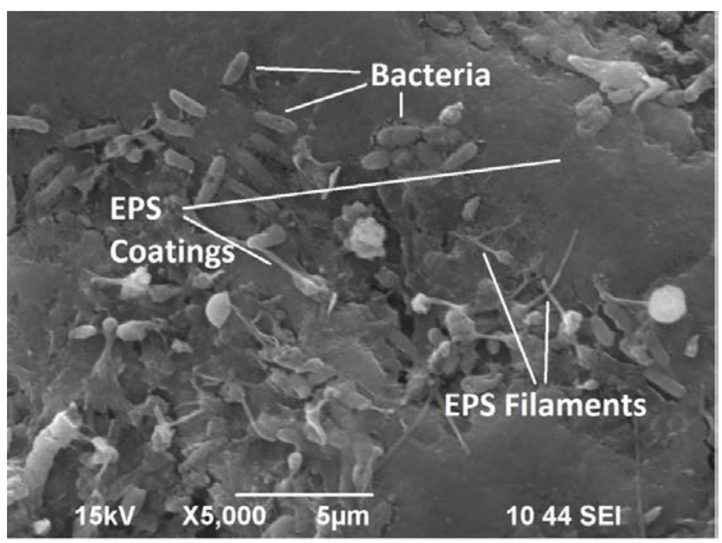

Fig. 7. Scanning electrical microscope picture showing biofilm is predominately Extracellular Polymeric Substances (EPS) formed by bacteria.

TABLE I. Metal concentrations in biofilm relative to bulk water

Analyte	Concentration in Biofilm	Typical Concentration in Injection Water	Units
Iron	49.9	0.43	mg/L
Manganese	27.6	0.15	mg/L
Cobalt	6.96	0.04	mg/L
Calcium	6.00	66	mg/L
Magnesium	3.95	23	mg/L
Zinc	1.87	0.03	mg/L

Dickinson et al. established the role of manganese-oxidizing bacteria (e.g., *Leptothrix discophora*) in mediating the oxidation of manganese on and around metal surfaces such as well screens [4]. They suspended stainless steel coupons in a culture of *Leptothrix disophora* and correlated the loss of soluble manganese and the concurrent increase in oxide precipitate on the steel surface. The precipitation was accompanied by chemical interaction between the manganese and the stainless steel coupons resulting in corrosion. In this mechanism, the Mn^{+2} and MnO_4 system is the likely redox couple. Microbial enzymes speed the otherwise stepwise two-electron reduction of Mn^{+2}. Mouchet points out that researchers do not know whether the bacteria use the metal redox couple as an energy source, or oxidize the iron and manganese to detoxify the ambient medium [5].

The magnification in cobalt concentration is notable. Lienemann et al. observed the relationship between cobalt and manganese and attributed it to the sorption of cobalt to manganese hydrous oxide and their redox driven interconversion between dissolved Mn and particulate Mn-oxides which is often mediated by microorganisms [6].

Mechanism of Fouling

The implications of these findings are that microbially-mediated oxidation of manganese may catalyze the corrosion of stainless steel and form corrosion byproducts. To be clear, there were no direct measurements of the microbes responsible for biologically-mediated oxidation of manganese. Rather this mechanism is based on the cited research of others and the chemical make-up of the biofilm (Table I) which shows iron, manganese, and cobalt have been concentrated in the biofilm relative to the bulk water.

Although our understanding of biologically-mediated corrosion chemistry is still evolving, it is clear that manganese precipitation and tuberculation can occlude well screens. It is suspected that the resulting precipitate is strongly bonded to the well screen making it difficult to remove and may be irreversible with current redevelopment techniques. It is also clear that carbon substrate is necessary to provide the biofilm collection point for the bacteria and metals to collect. Based on a careful evaluation of the information presented, the mechanism of fouling is theorized to be as follows:

- COD fuel biological growth and formation of EPS

- EPS chelates manganese iron and cobalt
- EPS starts clogging well screen
- Biologically-mediated oxidation precipitation of manganese dioxide and enoblement of stainless steel
- EPS is cleaned and washed away restoring some of the injection well capacity
- Manganese dioxide complexed with stainless steel surface remains causing irreversible fouling
- Well capacity mostly restored after redevelopment

CONCLUSIONS

Micronutrients are essential for the health of the bacteria used for biological treatment. Proper dosing is critical for the 200 West P&T system. Too little micronutrient results in excessive EPS formation that interferes with treatment. Too much micronutrient, especially manganese, fouls the wells decreasing injectivity. The proposed mechanism identifies two types of fouling:

- Biofilm fouling that is more severe, but is readily removed
- Manganese-based fouling that is more difficult to remove and may be irreversible.

Based on the information presented, the authors recommend that injection water contain less than 10 mg/L COD to limit biological growth (and the resulting biofilm) and less than 0.01 mg/L manganese to limit manganese-based corrosion of stainless steel well screens.

REFERENCES

1. Carlson, M., A. Menniti, K. Martins, H. Lee, J. Boltz, S. Simmons, J. Morse, M. Byrnes. The Importance of Micronutrients to Biological Treatment, 200 West Pump and Treat, Hanford Site, Richland, WA – 14021, Waste Management Conference 2014, Phoenix, Arizona (2014)
2. Stumm, W. and J. J. Morgan Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters, John Wiley & Sons, New York (1981)
3. Brown, M. and J. N. Lester. Role of bacterial extracellular polymers in metal uptake in pure bacterial culture and activated sludge—I. Effects of metal concentration. Water Research 16:11, 1539-1548 (1982)
4. Dickinson W. H., F. Caccavo Jr., B. Olesen, and Z. Lewandowski. Ennoblement of Stainless Steel by the Manganese-Depositing Bacterium *Leptothrix discophora*. Applied and Environmental Microbiology 63, 2502-2506 (1997)
5. Mouchet, P. From conventional to biological removal of iron and manganese in France. Journal American Water Works Association 84:4, 158-167 (1992)
6. Lienemann, C. P., M. Taillefert, D. Perret, and J. F. Gaillard. Association of cobalt and manganese in aquatic systems: Chemical and Microscopic Evidence. Geochimica et Cosmochimica Acta 61:7, 1437-1446 (1997)