

“IN SITU” GROUNDWATER TREATMENT

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Summary

High content of iron and manganese in groundwater has no negative effects on human health, but they often cause technical difficulties in public water supply systems, aesthetic quality problems for domestic users and complaints from industrial users.

Conventional methods for iron and manganese removal involve oxidizing processes. Nevertheless, the biological activity in the subsurface environment also produces significant transformations of these metals either directly or indirectly. Procedures for “in situ” removal of iron and manganese from groundwater, such as re-infiltration and the Vyredox® method described in this article, make use of this modern concept

developing an appropriate milieu for bacteria having the ability to metabolize iron and manganese and/or to increase the redox potential to oxidize reduced iron and manganese. Its wide application has been successful for small and medium-sized municipalities in Europe and America during the last three decades.

A moderate amount of nitrate is a harmless constituent of both food and water. However, high concentrations constitute a serious public health problem since nitrate may cause methemoglobinemia or blue baby syndrome in infants under six months of age. Unfortunately, nitrate in water has increased since pre-industrial times as human activities have accelerated the rate of fixed nitrogen being put into circulation.

Conventional methods for nitrate removal from groundwater are relatively expensive due to the investment, operating and maintenance costs. Since the early 1980s much attention has been paid to research concerning biological water treatment techniques based on the ability of denitrifying bacteria to reduce nitrates and nitrites to free nitrogen gas, which is harmless. Several methods have been investigated in the laboratory as well as “in situ” technologies like constructed wetlands and “in situ” bio-denitrification methods described in this article, but most methods are still in the experimental stages for municipal and/or commercial use.

1. Introduction

High content of iron, manganese and nitrate in groundwater often constitutes a serious problem in public water supplies systems for many small and medium-sized communities.

Iron and manganese have no negative effects on human health, but they cause technical difficulties such as clogging of water supply well screens and the water delivery pipelines, and taste and odour problems detectable at very low concentrations. Small amounts seriously affect the use of water for domestic purposes because iron and manganese in water stains plumbing fixtures and clothes during laundering, causing aesthetic water quality problems for the users. The presence of iron and manganese in a water supply may also cause complaints from industrial users (e.g. paper mills, petrochemicals, bottlers, textiles, commercial laundries).

The quality of groundwater often shows great spatial differences as the strata of soil and bedrock vary in space. Rainfall, melted snow and melted ice—depending on the latitude and the season—containing dissolved oxygen often infiltrate into the soil and percolate into the groundwater. Under such conditions, the groundwater content of iron and manganese is normally low. Nevertheless, if the stratum is less permeable due to the presence of clay layers or lenticular clay strata, the infiltration of water into the soil is reduced and the oxygen-rich surface water cannot always percolate deeper to recharge the groundwater. Then, the groundwater content of dissolved oxygen is low whereas the content of iron and manganese may be excessive. Such differences in quality (i.e. low or excessive iron and manganese content) have been observed in several aquifers where wells located within a short distance of each other have been drilled. However, these groundwater quality variations cannot be explained solely on the basis of the geological

and hydrological conditions, but also on physico-chemical factors and biological activity.

Nitrogen is vital to all existing living systems (i.e. plants and animals) to build many essential components such as proteins, vitamins, hormones and enzymes. Nitrate is a naturally occurring form of nitrogen found in the soil. A moderate amount of nitrate is a harmless constituent of both food and water. However, nitrate concentrations in surface waters such as streams and rivers are highly correlated with human population density and they have increased since pre-industrial times as human activities such as the use of fertilizers and atmospheric deposition have accelerated the rate of fixed nitrogen being put into circulation. Groundwater also shows increased concentrations of nitrate, where the major sources of contamination by nitrates are the use of fertilizers in many agricultural regions, seepage of septic tanks in areas lacking sanitation, unsuitable location and design of sanitary landfills and wastewater disposal ponds.

Nitrate constitutes a potentially serious public health problem, because high concentrations may cause methemoglobinemia or ‘blue baby syndrome’ in infants under six months of age. Nitrate in drinking water used to make the baby’s bottle is converted to nitrite in the stomach and is absorbed into the bloodstream, resulting in reduced oxygen supply to vital tissues, such as the brain. In extreme cases it can cause death. High ammonia concentrations tend to cause significant toxicity to fish and other organisms. Ammonia and nitrate are also important nutrients for the growth of algae, leading to eutrophication.

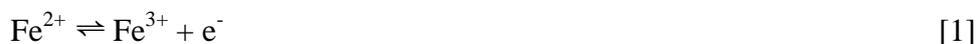
2. Origin, physicochemical factors and water regulations

2.1. Iron

Iron, a natural constituent of the earth’s crust, is one of the most abundant elements in sedimentary (~4.5%) and igneous rocks (~3.5%). Iron-bearing minerals and oxides impart a red or brown colour to sediments when deposited in an oxidizing environment and a grey colour where they are laid down in a reducing environment characterized by stagnant water and anoxic conditions such as a swamp or a lake bottom. Depending on geochemical conditions in the aquifer, groundwater percolating and flowing through the sediments can dissolve some of the iron from these minerals, giving the groundwater an iron content.

The presence of iron is also essential as a cellular component and for enzymatic processes in all life forms. Small amounts of about 2 to 3 mg iron per day are necessary for human health. However, only about 60 to 70% of the ingested iron is metabolized.

Iron generally occurs in two states of oxidation in nature, divalent (Fe^{2+}) ferrous ions and trivalent (Fe^{3+}) ferric ions. One state can be converted into the other by an exchange of electrons:



The reaction represented by equation [1] is referred to as an oxidation-reduction reaction (i.e. oxidation of divalent ferrous ions to trivalent ferric ions).

In environments with high content of dissolved oxygen, the trivalent state reacts with hydroxyl groups to form a solid precipitate:



Ferric hydroxide $[\text{Fe}(\text{OH})_3]$ is the dominating form of solid iron in natural aquatic systems. However, precipitated iron can also occur as iron sulphide (FeS) and ferrous carbonate (FeCO_3).

The overall reaction represented by equations [1] and [2] can be written as follows:



Therefore the divalent ferrous state is usually soluble, while the trivalent ferric state is insoluble. The stability in equation [3] depends not only on the activity of hydrogen ions (pH) but also by the activity of electrons which can be represented by the oxidation-reduction potential or redox potential, Eh .

The pH is a measure of hydrogen ion concentration in water. A pH of 7 is considered pure water or neutral. The water is basic or alkaline for pH values above 7 and acidic for pH values below 7. Redox potential, Eh, indicates whether the environment is oxidizing or reducing. Relatively high positive values of Eh indicate oxidizing conditions where iron is more likely to be precipitated. Low values of Eh indicate reducing conditions and iron is probably in solution. Eh is usually measured electrometrically in the field, with an electrode pair consisting of an inert metal electrode (e.g. platinum, gold) coupled with a reference electrode (generally a calomel electrode saturated with KCl).

The stability between the oxidized and reduced states of iron and manganese as a function of pH and Eh are shown graphically in Figure 1. The abscissa and the ordinate represent the pH of the water and the Eh in millivolts, respectively. The lower of the two sloping lines indicates equilibrium between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions. Its location is not completely stable as shown in Figure 1. Depending on the concentration of other elements in groundwater, it may vary a little. For all combinations of pH and Eh values under the line, the concentration of ferrous (soluble) iron is greater than the concentration of ferric (insoluble) iron. A combination of a pH value around 7 and an Eh value greater than + 230 mV is generally required to precipitate iron.

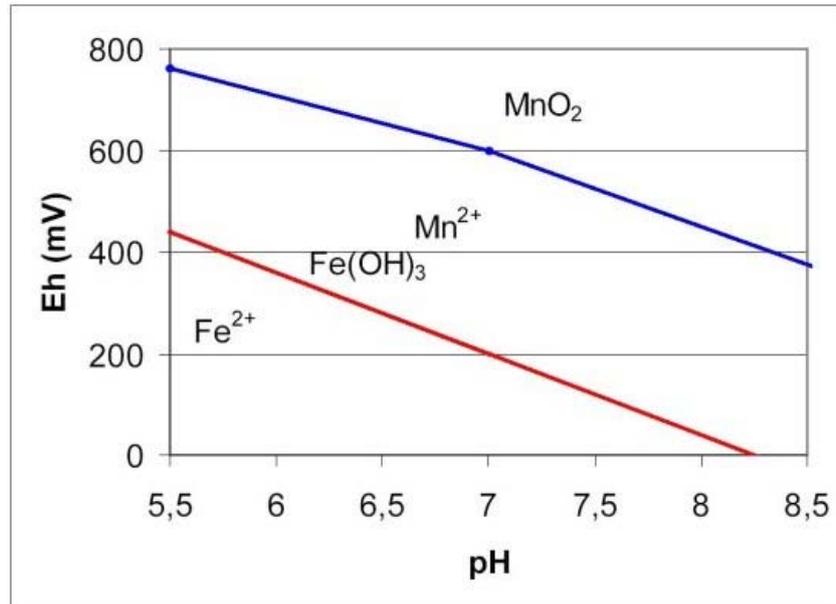


Figure 1. Simplified stability diagram for the oxidized and reduced states of iron and manganese as a function of pH and Eh

Iron concentrations of 1 to 10 mg/l in groundwater are common, but sometimes may reach concentrations up to 50 mg/l or uncommon even higher concentrations. The standards included in the Interim Secondary Drinking Water Regulations promulgated by the U.S. Environmental Protection Agency (EPA) as well as in the Guidelines for Drinking Water Quality from the World Health Organization (WHO) recommend for drinking water an iron content less than 0.3 mg/l. Some industrial processes, however, require that the iron content should not be greater than 0.1 mg/l. Groundwater with high iron content may be completely clear and colour less when pumped from the supply well. However, if the water is led to an open reservoir, upon standing for a time in contact with the oxygen in air may be sufficient to precipitate the dissolved iron. Then, the water begins to cloud up slightly and later rust coloured deposits may appear at the bottom of the reservoir.

Iron also occurs in inorganic and organic complexes in waters containing high concentrations of inorganic and organic substances. Examples of inorganic substances are silicates, phosphates or polyphosphates, sulphates and cyanides; whereas among the organic substances, humic, fulvic or tannic acids can be mentioned. Formation of inorganic and organic complexes act as inhibiting elements of the oxidation reaction producing a tendency to increased concentration of iron and manganese in solution which are more difficult to oxidize.

2.2. Manganese

Manganese usually occurs in two oxidation states as Mn^{4+} and Mn^{2+} . The chemical behaviour and occurrence of manganese in groundwater are similar to iron. Equation [4] shows the conversion of one state into the other by an exchange of electrons:



Manganese dioxide (MnO_2) in equation [4] is the dominant solid form of manganese in natural aquatic porous environments.

The upper sloping line in Figure 1 indicates equilibrium between divalent manganese (Mn^{2+}) and tetravalent manganese (Mn^{4+}). For all combinations of pH and Eh values above the upper sloping line, the concentration of both ferrous (soluble) iron and divalent (soluble) manganese is low. Thus, the groundwater is practically free from these metals.

Manganese is however less abundant than iron and, therefore, its concentration is normally much lower than iron. Nevertheless, manganese contents as high as 2 to 3 mg/l or unusually even higher amounts may be observed in water supply wells.

The standards of the Interim Secondary Drinking Water Regulations by the U.S. EPA for drinking water recommend a manganese content less than 0.05 mg/l whereas the Guidelines for Drinking Water Quality from the WHO recommend a maximum manganese concentration of 0.1 mg/l.

As well as iron, manganese also occurs in organic complexes which inhibit its oxidation.

2.3. Nitrogen

Unlike iron and manganese, which are derived from the mineral elements in sedimentary and igneous rocks, nitrate in groundwater mainly originates from the nitrogen cycle in the Earth's hydrosphere and biosphere. However, nitrogen is also found in geologic deposits such as organic materials in lignite and bituminous coal, clay and caliche soils. Nitrogen (N_2) comprises about 78% of the atmosphere. Most crop plants require large quantities of nitrogen to sustain high yields. Nevertheless, in general plants and animals cannot utilize free gaseous nitrogen directly from the air like they use carbon dioxide and oxygen. Instead, animals and plants utilize “fixed” nitrogen, which is combined with hydrogen or oxygen into inorganic compounds like nitrates or ammonia. The latter then dissolves and becomes ammonium.

Nitrogen fixation is mainly performed by soil bacteria (e.g. *Clostridium*, *Azotobacter* and *Rhizobia*). Plants assimilate and use fixed nitrogen from the soil to satisfy nutrient requirements, mainly during the growing season, and accumulate nitrate in their leaves and stems. The nitrate is subsequently transferred to the soil in a soluble form when the plant degrades. Animals in turn consume the plants and animal wastes return organic nitrogen to the soil as ammonia. The nitrifying bacteria (*Nitrosomonas*) oxidize the ammonia to nitrites, and *Nitrobacter* oxidizes the nitrite to nitrates, which can be exploited again by the plants. These processes constitute the cycle of fixation-decay-nitrification-fixation, which may continue indefinitely without any nitrogen return to the atmosphere .

In natural regions, plants normally make efficient use of available nitrate without any consequences for surface water and groundwater. In agricultural regions, however, nitrogen-based fertilizers (e.g. sodium nitrate, NaNO_3 , and potassium nitrate, KNO_3) are added to increase profitability and production. However, due to the extensive and uncontrolled use of fertilizers, the plants often cannot utilize all the nitrogen applied to the fields. Excess nitrate remains in the soil and dissolves into infiltrating water. The surplus nitrate is removed by percolating soil water and may leach into shallow groundwater or be washed off in surface and subsurface runoff into surface water bodies (e.g. streams, rivers and lakes). Nitrate in groundwater also originates from sewage waste (e.g. seepage from septic tanks in areas without sanitation, landfills and wastewater disposal ponds). Nitrate in surface waters often constitutes a serious problem in field crops where manure is used as a fertilizer. Thus, the presence of nitrate in groundwater and surface water may be regarded as evidence of contamination.

Nitrate tends to disperse with the groundwater without further attenuation. However, the denitrifying bacteria can reduce nitrates to gaseous nitrogen through a process known as denitrification, which occurs under anoxic conditions. Nevertheless, denitrification is not common in well-cultivated soils.

The principal water quality criteria for nitrogen focus on nitrate and ammonia. The standards of the U.S. EPA for drinking water recommend a nitrate content less than 45 mg/l, which is equivalent to 10 mg/l of elemental nitrogen (N) whereas the WHO guidelines for drinking water quality recommend a maximum nitrate concentration of 50 mg/l. Nitrate in concentrations above these limits is unsuitable in drinking water supply due to its potentially serious toxic effect on public health. Concentrations higher than 45-50 mg/l may cause methemoglobinemia (blue baby syndrome) in infants under six months of age. High ammonia concentration tends to cause significant toxicity to fish and other organisms. Ammonia and nitrate are also important nutrients for the growth of algae. Excessive nitrogen in groundwater discharging into surface waters (e.g. rivers and lakes) can therefore lead to eutrophication.

3. Biological oxidation and reduction

The oxidation of iron and manganese is not only an inorganic reaction. Biological activity in the subsurface environment—which may have been occurring for the last three billion years—produces significant geochemical modifications. The reactions and transformations of iron and manganese are an example. Many bacterial processes are inter-related with such transformations either directly or indirectly. Some kinds of bacteria have the ability to metabolize iron and manganese and/or to increase the redox potential to the required level to oxidize reduced iron and manganese. In other cases, the decomposition of organic substance by heterotrophic bacteria consumes oxygen dissolved in water and thus decreases the redox potential to a level where the trivalent ferric iron becomes reduced to divalent ferrous iron.

Denitrification is one of the main processes in the nitrogen cycle. The denitrifying bacteria have the capability to reduce nitrates and nitrites to free nitrogen gas and nitrogen oxides. Since the denitrifying bacteria require organic carbon as an energy source, denitrification occurs primarily in soils where organic matter is easily available.

The reaction occurs under anoxic conditions, i.e. the absence of oxygen, where the denitrifying bacteria use nitrate or nitrite for respiration instead of oxygen.

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Biographical Sketch

Luis Silveira was born in Montevideo, Uruguay in April, 1949. He started to study engineering in his native country, but in 1974 he fled from the military regime and arrived in Sweden, where he obtained political refugee status. After learning Swedish, he resumed his studies. He became a Swedish citizen in 1978. Next year, he obtained a M.Sc. degree in Hydraulics and Environmental Engineering, at the Royal Institute of Technology, in Stockholm, Sweden. After his graduation, he started to work with groundwater in a Swedish consulting and constructing firm. In 1980, he took a six-month international postgraduate course in Barcelona, Spain, for deepening his knowledge of groundwater hydrology. Back in Stockholm, he pursued working with groundwater projects in Scandinavia as well as at an international level.

With the return of democracy, he moved back to Uruguay in 1988. There he joined the Hydrology Group at the IMFIA (Department of Fluid Mechanics and Environmental Engineering), Faculty of Engineering, University of the Uruguay Republic. Over the last fourteen years he has lectured in Surface Hydrology and Groundwater Hydrology and worked with several applied research projects concerning both surface hydrology and groundwater. During this activity he established a cooperation programme with the Royal Institute of Technology to strengthen the human resources from IMFIA. Then, he continued his postgraduate studies and finally he defended his Ph.D. thesis about “Hydrological Modelling of Natural Grasslands with Small Slopes in Temperate Zones” in 1998, at the Royal Institute of Technology, in Stockholm, Sweden. Today, he is Titular Professor and head of the Hydrology Group. His main academic and professional interests are chemical-biological techniques for “in situ” groundwater treatment, hydrological modelling of both surface water and groundwater, hydrology of flatlands, forest and urban hydrology, hydrological applications of multivariate analysis and integrated water resources management.

He likes to listen to classical jazz and instrumental tango music while he performs his research work. In his free time he likes to read fiction books, see movies, especially European ones, as well as to enjoy his child Sebastián and his wife Patricia.