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IRON - THE ENVIRONMENTAL IMPACT OF A UNIVERSAL ELEMENT

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Iron is a common constituent in soils and groundwater. It readily participates in subsurface redox reactions and under some conditions can cause problems with groundwater remediation systems. The purpose of this column is provide a broader setting for the impact of iron chemistry on groundwater.

BACKGROUND

The average crustal abundance of iron is 5% by weight. The iron content of soils is typically in the range of 0.5% to 5%, and is dependent upon the source rocks from which the soil was derived, transport mechanisms, and overall geochemical history.

Not only is iron common, but it is also reactive and readily reflects changes in surrounding [Eh/pH conditions](#). This is particularly true in soil and groundwater systems that have been environmentally impacted with hydrocarbons. In groundwater systems iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{+2}) or oxidized insoluble trivalent ferric iron (Fe^{+3}). The modern atmosphere has 21% oxygen, causing most of the iron in shallow subsurface soils to be in the oxidized ferric state.

Ferric hydroxide ($\text{Fe}(\text{OH})_3$) is the direct result of ferrous iron oxidation and precipitation. With time, ferric hydroxide is mineralized. The principal forms of mineralized ferric iron found in soils are:

- amorphous hydrous ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$),
- maghemite ($\gamma\text{-Fe}_2\text{O}_3$),
- lepidocrocite ($\gamma\text{-FeOOH}$),
- hematite ($\alpha\text{-Fe}_2\text{O}_3$), and
- goethite ($\alpha\text{-FeOOH}$).

The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing Eh conditions has a solubility of 0.6 $\mu\text{g/L}$, which is three orders of magnitude greater than that of goethite. However, high concentrations of iron in groundwater is not rare. Obviously, other processes are at work.

IRON COMPLEXING

Ferrous iron is soluble as a cation, ferric iron is not. However, ferric iron can form soluble complexes with many inorganic and organic ligands, including compounds that are the byproducts of the biodegradation of aromatic petroleum hydrocarbons (catechols, which are organic acids resulting from aromatic ring cleavage). The yellow/orange coloration of groundwater at some sites contaminated with

petroleum hydrocarbons is due to these ferric-catechol complexes.

It is important to remember that complexed ions typically react more slowly than uncomplexed ions. This impacts the behavior of ferrous iron. Ferrous iron normally can be oxidized to ferric iron in minutes (see below for more details). Complexed ferrous iron may take months to complete the same reaction. This has profound implications for the fouling of groundwater injection systems.

Humic acid, fulvic acid and tannic acid are examples on non-contaminant organic complexes. Phosphate also serves as a very effective complexing agent for iron.

IRON OXIDATION

The time required for uncomplexed ferrous iron to undergo oxidation to the ferric state is dependent on many factors, the dominant being: pH; temperature; dissolved oxygen level; and the presence of other soluble ions. The lower the pH and temperature the longer the time required for completion of the oxidation reaction. Increasing dissolved oxygen decreases the time required for oxidation. For example:

- At pH 7.0, 90% Fe^{+2} oxidation requires 1 hour at 21° C and
 - 10 hours at 5° C. At 21° C
- At pH 8.0, 90% Fe^{+2} oxidation occurs in 30 seconds,
- at pH 6.0 it requires 100 hours.
- The critical dissolved oxygen concentration is 2 mg/L. Below that ferrous iron oxidation occurs slowly.

The above reactions are often responsible for the iron fouling of air strippers treating iron rich groundwater. These reactions can also foul screens in poorly designed recovery wells pumping that groundwater.

MICROBIOLOGY AND IRON

Iron readily undergoes reduction or oxidation, depending upon surrounding conditions. As a consequence there are many microbiological metabolic pathways that utilize **redox couples** between ferrous and ferric iron. Organic material can be biodegraded with ferric iron as the terminal electron acceptor, resulting in the production of reduced soluble ferrous iron. Anaerobic conditions are required as is the presence of ferric iron in a suitable form. As the crystallinity of the ferric iron mineral increases (as discussed above) the microbiological availability decreases. Or contrarily, iron fixing bacteria can oxidize ferrous iron to ferric iron, even under oxygen poor conditions, by many methods including: the extraction of carbon dioxide (for microbial energy systems) from ferrous bicarbonate leaving insoluble ferric hydroxide; and the utilization of iron bearing organic acid complexes as a carbon source, leaving precipitated ferric hydroxide. These are the reactions that are typically responsible for iron fouling of well screens, piping systems and air strippers that are used to remediate iron rich groundwater.

IRON OXIDES AND IN-SITU METAL/ORGANIC ADSORPTION

Amorphous hydrous ferric oxide can be described as an amphoteric ion exchange media, meaning that as pH conditions change it has the capacity to offer hydrogen ions (H^+) or hydroxyl ions (OH^-) for cation or anion exchange respectively. As a rough rule of thumb amorphous ferric oxide is capable of adsorbing 0.5 milli moles of ionic material per gram. Ionic material includes: oxyanions of chrome, arsenic or selenium; heavy metal cations; or ionized organic compounds. The dominant mechanism of interaction between iron oxides and soluble organic compounds is through carboxyl and hydroxyl functional groups on the organic. This is particularly true for the organic acids that are the intermediate product of the biodegradation of petroleum hydrocarbons.

Sorption behavior is primarily related to pH (within the typical range of 5.0 to 8.0) and each ion has its own optimum pH range for adsorption. Given the average concentration in soil, the iron in a cubic yard of soil is capable of adsorbing from 0.5 to 5 pounds of soluble metals as cations, anionic complexes, or a similar amount of organic biodegradation products.

SUMMARY

The reactions described above are complex. At any given location it is difficult to determine the specific processes taking place. However, the overall effect is as follows: Impacting hydrocarbons provide a carbon source to stimulate aerobic microbial degradation. This consumes the readily available oxygen driving the system anoxic. In the anoxic state soluble ferrous ions are generated and soluble ferrous and ferric complexes are formed. High levels of soluble iron is an indicative side effect of hydrocarbon contamination in groundwater.

The mobilized iron is then drawn into installed groundwater recovery and treatment systems. There, oxygenation takes place changing redox conditions, the elevated levels of soluble iron react and precipitate, causing fouling in the recovery and treatment systems.

Adsorption and attenuation of [contaminant transport](#) is concurrently taking place on the residual solid iron oxide phases remaining in the soil matrix. This can extend the duration of a pump and treat effort. Or it can be exploited in a "flume and gate" [groundwater barrier system](#).

Irrespective, pay attention to iron in groundwater, its presence and form are indicators of complex reactions in the subsurface. This is information to be exploited rather than ignored.

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