IRON OXIDATION AND IRON BACTERIA FORMATION IN MUNICIPAL PRODUCTION WELLS IN SUFFOLK COUNTY, NEW YORK

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ABSTRACT

The continuing problem of attempting to restore the lost capacities of clogged and/or biofouled municipal water supply wells in Suffolk County has led to extensive research as to the underlying causes of the problem. In particular, the geochemical and biological phenomena relating to ferrous iron oxidation and iron bacteria growth in deeper Magothy aquifer supply wells have been investigated. The construction of municipal production wells screened in the deep Magothy aquifer presents an ideal opportunity for accelerated dissolution of iron minerals (such as iron oxides and iron hydroxides) and precipitation at the well intake. Additionally, iron related bacteria are quite common throughout Long Island's groundwater environment, and have been found in cores of deep Magothy sediments prior to well construction. Iron bacteria are able to survive in this environment until more favorable conditions (such as near a pumping well) are encountered.

The problem of clogging and biofouling appears to be due to a variety of geochemical and biological causes which have been approached in a piecemeal fashion by most municipal water suppliers in their attempts to restore the productivity of such wells. In this paper, equilibrium thermodynamic modeling is used to constrain the possible sources of iron to wells, evaluate the theoretical maximum amount of iron that may precipitate at a well intake under realistic conditions, and also provide an interpretation of geochemical behavior observed in the field. A brief overview of the interaction of iron bacteria in the subsurface geochemical environment, including a field example, will also be examined.

BACKGROUND

In the Magothy aquifer, conditions most favorable to well clogging occur near discharge zones (Walter, USGS personal communication, 1991). These areas include the far south shore of central and western Suffolk County, between potentiometric highs in the central part of Suffolk County, and the far western and far eastern parts of the south fork (see Figure 1). Experience reconditioning clogged wells bears this out, at least qualitatively.



Magothy discharge zones have the following water quality characteristics: elevated levels of iron and phosphorous, low pH, and low levels of dissolved oxygen (DO). In addition, these portions of the Magothy tend to have abundant pyrite and lignite, and the sediments tend to be finer grained. Based on operational experience, these water quality characteristics appear to be responsible, at least in part, for the increased likelihood of wells clogging due to inorganic

iron hydroxide precipitation or iron bacterial biofouling, or a combination of the two. Well clogging and biofouling problems also occur in wells screened in the upper Glacial aquifer. However, this paper will concentrate on the Magothy aquifer.

Previous studies conducted for the Suffolk County Water Authority have shown different dissolved iron concentrations for Magothy aquifer sections in which a test boring was constructed prior to the construction of a

permanent well (Leggette, Brashears, and Graham, Inc., 1980). These data reveal that iron concentrations for both test borings and production wells are much higher on the south shore than for the other two regions, and also that iron concentrations are lower for production wells than for test borings, even when the wells are screened in the same aquifer sections. This indicates that iron is precipitated before it enters the production well.

BEHAVIOR OF IRON IN THE SUBSURFACE

Precipitation initially entering the groundwater system of Long Island is usually high in dissolved oxygen from the atmosphere. As the water flows from the divide southward and deeper, (e.g. into the Magothy aquifer), it loses DO. The DO concentration approaches zero at some point, possibly offshore. A well screened in these low DO sediments can alter the natural geochemical sequence of events by serving as a conduit to the surface, allowing for mixing of oxygen-poor groundwater from the Magothy aquifer and oxygen-rich shallow groundwater. In southwestern Suffolk County, mixing may be occurring due to a regional drawdown of shallow, oxygen-rich groundwater as a result of heavy pumpage by water suppliers (Walter, USGS, written communication, 1993). In the presence of iron bearing minerals such as pyrite and hematite (found naturally in Magothy sediments on the south shore), this mixing can allow for initial dissolution of large quantities of iron, and later precipitation of almost all of it at the well intake. Additionally, the pumping of water from the well constantly brings in "new water" for these reactions to continue (under non pumping conditions, where groundwater moves at the rate of .5 to 1 foot per day, this process would happen very slowly). The above mentioned scenario was modeled using *PHREEQE* to better quantify the dissolution and precipitation of iron in the Magothy aquifer.

MASS TRANSFER MODELING OF IRON IN THE MAGOTHY AQUIFER

Geochemical modeling using the *PHREEQE* software was conducted in an attempt to discover the theoretical maximum amount of iron that can be initially dissolved and then precipitated at a well intake, under typical field conditions. In the *PHREEQE* simulations, the geochemistry as it affects the dissolution and precipitation of the iron bearing minerals pyrite and hematite was modeled in the following manner. In "Step 1", water entering the system was given a "high" initial DO concentration (anywhere from 1 to 6 ppm), and was equilibrated with pyrite and hematite. The amount of each mineral capable of dissolving at each DO concentration was calculated. In Step 2, this solution was then allowed to react with varying (but lower) amounts of DO (anywhere from .1 ppm to 3.2 ppm), similar to what would be encountered in a deep well. The amount of iron which would precipitate out of solution as amorphous ferric hydroxide, Fe(OH)₃, was again calculated.

				STEP 1 02 CONC.		(INFLUENT)					
		3.13E-05		6.25E-05		9.38E-05		1.40E-04		1.87E-04	
		(1 ppm)		(2 ppm)		(3 ppm)		(4.5 ppm)		(6 ppm)	
	1.00E-04	Step 1 Pyrite	1.03E-05	Step 1 Pyrite	1.91E-05	Step 1 Pyrite	2.80E-05	Step 1 Pyrite	4.15E-05	Step 1 Pyrite	5.53E-05
	(3.2 ppm)	Step 1 Hematite	9.90E-08	Step 1 Hematite	9.28E-05	Step 1 Hematite	9.34E-06	Step 1 Hematite	1.06E-05	Step 1 Hematite	1.31E-05
		Step 2 Fe(OH)3	3.00E-05	Step 2 Fe(OH)3	3.76E-05	Step 2 Fe(OH)3	4.66E-05	Step 2 Fe(OH)3	8.21E-05	Step 2 Fe(OH)3	7.90E-05
		Step 1 Pyrite	1.03E-05	Step 1 Pyrite	1.91E-05	Step 1 Pyrite	2.80E-05	Step 1 Pyrite	4.15E-05	Step 1 Pyrite	5.53E-05
2	3.13E-05	Step 1 Hematite	9.90E-06	Step 1 Hematite	9.28E-05	Step 1 Hematite	9.34E-06	Step 1 Hematite	1.08E-05	Step 1 Hematite	1.31E-05
-	(1 ppm)	Step 2 Fe(OH)3	3.00E-05	Step 2 Fe(OH)3	3.78E-05	Step 2 Fe(OH)3	4.66E-05	Step 2 Fe(OH)3	6.21E-05	Step 2 Fe(OH)3	7.90E-05
2										(.9 ppm)	
								(.8 ppm)		Pyrite	
۵.						(.65 ppm)		Pyrite		Step 1 Hematite	5.53E-05
ш	1.1.1.1			(4 ppm)		Pyrite		Step 1 Hematite	4.15E-05	Step 1 Fe(OH)3	1.31E-05
-	"Inter-	(.25 ppm)		Pyrite		Step 1 Hematite	2.80E-05	Step 1 Fe(OH)3	1.06E-05	Step 2	7.90E-05
s	mediate"	Pyrite		Step 1 Hematite	1.91E-05	Step 1 Fe(OH)3	9.34E-08	Step 2	8.21E-05		
	Solutions	Step 1 Hematite	1.03E-05	Step 1 Fe(OH)3	9.28E-05	Step 2	4.66E-05				
	(Step 2 02)	Step 1 Fe(OH)3	9.90E-06	Step 2	3.78E-05						
		Step 2	3.00E-05								
		Pyrite		Pyrite		Pyrite		Pyrite		Pyrite	
	3.13E-06	Step 1 Hematite	1.03E-05	Step 1 Hematite	1.91E-05	Step 1 Hematite	2.80E-05	Step 1 Hematite	4.15E-05	Step 1 Hematite	5.53E-05
	(.1 ppm)	Step 1 Fe(OH)3	9.90E-06	Step 1 Fe(OH)3	9.28E-05	Step 1 Fe(OH)3	9.34E-06	Step 1 Fe(OH)3	1.08E-05	Step 1 Fe(OH)3	1.31E-05
		Step 2	1.24E-05								
	Source: Colabuf	o, 1993, p. 10									

TABLE 1. DISSOLUTION AND PRECIPITATION OF IRON SPECIES AT DIFFERENT DO CONCENTRATIONS

Modeling runs were also attempted using pyrite alone and hematite alone, but proved to be unrealistic. In the simulations using hematite alone, not enough iron was dissolved to simulate known conditions. In the simulations using pyrite alone, the pH dropped to extremely low levels (approximately 4.0). Pyrite and hematite were both required in order to emulate actual field conditions (i.e. pH) encountered. Hematite essentially buffers the pH to more realistic levels. Only equilibrium modeling was attempted. The actual rates for the reactions, as well as the catalyzing effects of iron bacteria, were not the focus of these simulations.

The results obtained from the modeling runs are summarized in Table 1. Each Step 1 initial DO concentration allows for a particular dissolution of pyrite and hematite. The concentrations varied from 1.03×10^{-5} mol (pyrite) and 9.9×10^{-6} mol (hematite) at 1 ppm of DO to 5.53×10^{-5} mol and 1.31×10^{-5} mol, respectively, at a Step 1 DO concentration of 6 ppm. For any Step 2 DO concentration above .1 ppm (3.13 $\times 10^{-6}$ mol), virtually <u>all</u> of the dissolved iron will precipitate out of solution. Only when Step 2 DO concentrations approach the lower limit of .1 ppm is the amount of Fe(OH)₃ precipitated out of solution limited, regardless of the initial Step 1 DO concentration.

The most likely manner in which the Step 2 dissolved oxygen could reach the deeper Magothy aquifer would be by vertical percolation along the well casing, or by recharge of more oxygen-rich waters from above the well screen. Additionally, dissolved oxygen *per se* does not have to be present. If some other oxidant, such as nitrate or sulfate, is present, the geochemical behavior should proceed as modeled (although the actual quantities of each mineral dissolved and precipitated would vary). This means that large amounts of iron (i.e. as much as 10 kg/day under normal operating conditions) can precipitate out of solution at a well intake or on the pump column , resulting in the accumulation of up to 6 cm/year of iron precipitate on a well screen under these conditions (Colabufo, 1993).

IRON BACTERIA

Iron bacteria accentuate the previously described problems involved in operating municipal water supply wells. These bacteria are well documented throughout the groundwater industry by well drillers, water plant operators, engineers and scientists, but have only been understood very recently. The Suffolk County Water Authority has extensive experience in dealing with wells clogged by iron related bacteria and their related iron deposits, spending an average of approximately \$400,000 per year on well reconditioning.

Iron bacteria can be defined as bacteria which are able to assimilate the oxides and hydroxides of iron and manganese into their extra cellular material and/or within the cell material itself (Cullimore, 1986). These bacteria have been found in environments as diverse as deep sea hydrothermal vents, desert rocks, swamps, and, of course, well intakes. Iron bacteria can be grouped into two categories based upon the way in which they induce the precipitation of iron (Driscoll, 1986). One group enzymatically catalyzes the oxidation of iron and manganese and uses the energy to promote the growth of a threadlike slime, or biomass. Large amounts of ferric hydroxide can accumulate on the biomass. In this process, the bacteria obtain energy by oxidizing ferrous iron to ferric iron. The second group of iron bacteria induces iron precipitation by non enzymatic methods. These organisms promote precipitation by increasing the pH of the water, by altering the redox potential of the water, or by liberating chelated iron (Driscoll, 1986).

Iron bacteria grow and develop around a well in a multi-step process. Cells live in the aquifer and subsist on carbon found therein, such as lignite, or in some cases inorganic CO₂. Under environmental stresses, these microbes can shed their excess cellular material and become very small (i.e. .1 to .3 microns)(Cullimore, 1986). At this size, they can fit into the interstitial spaces between grains of aquifer material and travel great distances at the prevailing groundwater velocity. Free floating organisms such as these are know as <u>planktonic</u> organisms. Under further environmental stress, these bacteria may enter a state of semi-suspended animation (these are known as <u>ultra micro cells</u>). Reactivation of the organisms occurs when more favorable environmental conditions return. Aquifers at one time were thought to be sterile and void of any bacteria, including iron bacteria. However, a recent cooperative study between the USGS and the SCWA found iron bacteria cells in core samples of deep Magothy sediments taken prior to the construction of a well.

Incrustation of a well intake is caused by an accumulation of a biomass consisting of iron bacteria, inorganic precipitates of iron hydroxides, and material known as Extra Cellular Polymeric Substances, or ECPS. ECPS consists of polysaccharides and glycoproteins (Sutherland, 1983). When a well is drilled into the subsurface and begins pumping groundwater, conditions change toward a more favorable environment for iron bacteria. An oxidation zone forms in response to groundwater flow conditions. This oxidation zone allows for increased growth of aerobic organisms, which can attach to solid surfaces (i.e. well screens) in the form of a biofilm. These attached organisms are referred to as <u>sessile</u> organisms. In the sessile state, nutrient-rich groundwater flows past the organism, allowing for growth and development of an extensive biofilm.

As the biomass grows, water quality changes may result. Such changes include removal of iron and manganese, and increased turbidity due to turbulent flow. Increased turbulence may increase nutrient exposure and accelerate biofilm growth. This may explain why many relatively low iron wells at the SCWA have become clogged over the years, and why reconditioning and redrilling serves to increase the iron concentration of the produced water, occasionally rendering the well unusable. Another water quality change that is poorly documented is the removal of organic pollutants from groundwater by the iron bacteria. This may be beneficial in aquifer remediation problems. The end result of iron bacteria activity in the vicinity of a well could be that the water sampled from a well could be of much different quality than the native groundwater in the aquifer.

Conditions conducive to the growth of iron bacteria in wells are found throughout Long Island. These conditions are: pH of from 6.0 to 10.0; total iron concentration of .01 to 4.0 ppm; dissolved oxygen of .5 to 4.0 ppm, and temperature of 40° to 60° F (Smith, 1980). A typical Suffolk County Water Authority well meets all of these conditions: a slightly acidic pH of 6 to 6.5; total iron of .1 to .7 ppm; a temperature of approximately 52° F., and a DO concentration of anywhere from 1 to over 9 ppm (Walter, USGS, written communication, 1991).

Numerous other chemical factors are known to affect the biofouling potential of a well. The most important are phosphorous, oxygen, nitrogen, and iron (Cullimore, 1986). Phosphorous is important due to its role in the storage of energy within cells. In systems with mostly planktonic bacteria, the concentration of phosphorous able to support a sizable bacteria population is considered to be between .05 and .5 mg/L. In a well, where sessile bacteria predominate, this critical concentration is probably much lower, since water continuously flows past the organism. Phosphorous can also be introduced into a well after it goes into operation, by using phosphate compounds in an attempt to sequester the dissolved iron and keep it from precipitating.

Oxygen is of critical importance with regard to the rate at which biofouling occurs. The literature suggests that the critical concentration for initiation of aerobic microbial activity is between 20 and 200 micrograms O_2/L , with maximum aerobic growth occurring at a concentration of 3 mg O_2/L . Mansuy (1986) found that an anaerobic environment would produce approximately 18% of the rate of well clogging compared to an aerobic environment. Most SCWA wells have dissolved oxygen concentration ranging from less than 1 mg/L to approximately 9 mg/L (Walter, USGS, written communication, 1991).

High nitrate concentrations indicate an increased biofouling potential, according to Cullimore. In certain situations, aerobic organisms may utilize nitrate as an alternative to oxygen for respiration. This may have some significance relative to the reactions modeled in the previous section of this report. Nitrate respiration can lead to significant biofouling even in an oxygen-free environment. This would probably be a more significant factor for irrigation and domestic wells, which typically have nitrate concentrations much higher than public supply wells, especially those screened in the Magothy aquifer.

The total iron concentration of groundwater is a very important factor affecting biofouling potential in a well. The critical concentration is between .1 and 10 mg/L. SCWA wells commonly have total iron concentration of from less than .1 mg/L to as high as 1.5 mg/L. At the lower concentrations, flow takes on a greater importance, due to the ability of the biomass to assimilate nutrients as the water flows past it. However, as stated previously, the iron concentration obtained from sampling a well may be quite different from the actual iron concentration of native aquifer water due to the effects of the iron bacteria. Therefore, it may be very difficult if not impossible to determine the exact iron concentration of the native aquifer water by conventional means.

Manganese also plays an important role. The presence of as little as .5 mg/L of manganese can lead to accelerated growth of iron bacteria (Cullimore, 1986).

The effects of iron bacteria on water quality (particularly iron concentration) were observed during an investigation of reconditioned SCWA wells. All wells investigated had iron bacteria (mostly Galleonella) present to some extent on the pump column. In almost all cases, the total and dissolved iron concentrations increased after reconditioning, indicating that iron bacteria, present in greater numbers prior to reconditioning, were taking iron out of solution and incorporating it into their biomass.

Operational practices were found to be the reason for biofouling and clogging of numerous SCWA wells. For many years, the standard practice at the Suffolk County Water Authority for high iron wells was to treat them with Sodium Hexametaphosphate (a.k.a. "Calgon") in order to sequester the iron and keep it from precipitating. The Calgon solution was fed directly into the well via a 1/4" diameter plastic tube running down the pump column. The solution would then get thoroughly mixed with water as it passed through the pump impellers and into the distribution system. Unfortunately, many wells treated in this manner have become so permanently clogged with iron bacteria that they can no longer be used. This method of phosphate injection has been

eliminated. Instead, the Calgon injection tube is located near the check valve on the discharge piping. This allows for a sufficient mixing of the chemical with the water, but does not allow the chemical to backfeed down the well.

Most of the SCWA's chronically clogged, problem wells are located in southwestern Suffolk County, a groundwater discharge area that is higher in phosphorous to than recharge areas (Walter, USGS, verbal communication, 1991). The correlation of biofouled, Calgon-fed wells in southwestern Suffolk to the presence of iron bacteria is undeniable.

A well's operational and flow characteristics can also influence its clogging behavior. Operational experience has shown that a biofouled well can be pumped for more total hours if it is pumped continuously than if pumped intermittently. Intermittent pumping allows for mixing and oxygenation of waters when the well recovers, which could lead to iron oxidation and accelerated biofilm growth. Possibly the worst condition for well biofouling is a non pumping well (such as an observation or monitor well) in a nutrient rich groundwater environment. The biofilm may expand rapidly as it seeks nutrients elsewhere. Abundant anecdotal evidence exists regarding the chronic biofouling of wells near aquifer remediation sites. For municipal supply wells, the practice of using system water for prelubrication of the well pump during idle periods may also contribute to biofouling. The prelube water is often treated water from the distribution system and is higher in pH and DO than native groundwater. The introduction of water of higher pH and DO into a well with higher iron and lower pH could accelerate the growth of biofilm on the well screen and in the gravel pack.

FIELD EXAMPLE: REDRILL OF A SCWA PRODUCTION WELL

In the redrill process, the screen of an existing production well is removed, the aquifer surrounding to the screen is drilled out, and a new screen and gravel pack is installed in the well. The objective is usually to restore the capacity of an older well after many years of well screen clogging. Wells on which this procedure is performed usually have a long history of clogging and/or biofouling. The Suffolk County Water Authority's Harvest Lane Well No. 3 was recently redrilled, with some interesting and unexpected results.

Harvest Lane Well No. 3 was constructed in 1971. Original water quality was excellent, with total iron measuring .1 mg/L. The original specific capacity of the well was $59.2 \text{ gpm/}_{\text{ft}}$ of drawdown. The well continued to operate efficiently until 1988, when it became severely clogged and required reconditioning. Subsequent reconditioning treatments yielded progressively worse results. Figure 2 shows this trend. In late 1991, it was decided to redrill this well in hopes of restoring its lost capacity. Since iron concentrations were not too high, no water quality problems were foreseen. Upon completion of the redrill in January of 1992, the specific capacity was $53 \text{ gpm/}_{\text{ft}}$ of drawdown (vs. 10.8 prior to redrilling), and the project was deemed a success. However, the dissolved iron concentration had risen to almost 2 mg/L, the pH had decreased to 4.66, and a strong odor of hydrogen sulfide gas was detected. Also noteworthy was the extraordinarily high DO concentration of 4.7 mg/L (vs. less than 1 mg/L for a typical well in this part of the Magothy). The most reasonable explanation for this behavior is the oxidation of pyrite. This would account for the decreased pH and the marked increase in total iron concentration.



The increase in DO is most likely the result of field sampling errors. The presence of hydrogen sulfide should insure a very low DO concentration. However, hydrogen sulfide odors have often been reported in well waters with measurable dissolved oxygen. The presence of hydrogen sulfide and DO could be due to a state of disequilibrium, possibly resulting from the previously-mentioned regional drawdown of shallower groundwater or of vertical percolation along the well casing (Walter, USGS, written communication, 1993).

A closer look at the mechanics of pyrite oxidation can help to explain what happened. Recirculating and recharging distribution system water down a well (as is done during a typical redrill) would result in increased Eh of the water in the screen zone of the well. This is undoubtedly the main reason why no early warning is given by problem wells. If only dissolved iron is analyzed, and the thermodynamics are such that the precipitation of ferric hydroxide is favored, this phenomenon will go undetected by water quality analysis alone.

Another piece of evidence to support the above model as being the reason for the observed behavior of Harvest Lane Well No. 3 was its post redrill geochemical behavior. After test pumping confirmed the high dissolved iron concentration, the well lay idle for approximately four months. During that time, the iron concentration decreased to approximately 1.13 mg/L. The well was then pumped and sampled 24 hours a day for approximately 1 week. During that time interval, the dissolved iron concentration declined further to approximately .5 mg/L, lending credence to the belief that the increase in iron was caused by the oxidizing effects of the recirculated water on pyrite present in the aquifer. Apparently, once the recirculated water was pumped out of the aquifer, the water returned to background levels.

CONCLUSION

Conditions on Long Island conducive to the clogging of wells by iron oxide precipitation and/or iron bacteria biofouling are most common in wells located on the south shore screened in the Magothy aquifer. These conditions include low pH, low dissolved oxygen, high iron and phosphorous, and the presence of lignite and pyrite in the aquifer. According to geochemical modeling, high DO recharge water entering the groundwater system can dissolve large quantities of pyrite and hematite from the Magothy sediments. These minerals can precipitate out of solution when later mixed with even small concentrations of DO, such as is found near pumping wells. Prolonged well pumpage can permanently alter the subsurface geochemistry and ultimately the quality of the water produced by a well.

Iron bacteria biofouling is a related problem plaguing south shore Magothy wells on Long Island. Iron bacteria have been observed in sediment samples of Magothy aquifer material prior to well construction. Long Island groundwater is ideally suited to the growth and development of iron bacteria. These organisms can clog well screens and can alter native water quality by catalyzing iron precipitation under otherwise kinetically unfavorable conditions. Well reconditioning treatments to restore lost capacity also can temporarily alter the geochemistry of the aquifer in the vicinity of the well.

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