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The Solubility of Ferric Oxyhydroxides in Natural Waters

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ABSTRACT

Iron in ground water is often present both in solution and as suspended ferric oxyhydroxides. In most instances amounts of dissolved iron in natural waters are limited by solubility of the ferric oxyhydroxides, whether suspended or present as part of aquifer materials. Oxyhydroxide solubilities, which range widely in natural waters, may be described by $pQ = -\log [Fe^{3+}] [OH^-]^3$, where $[Fe^{3+}] [OH^-]^3$ is the product of ion activities in the water. pQ values calculated from Fe(II), Eh, and pH measurements in several types of high iron ground and surface waters (Fe(II) = 0.02 to 1460 ppm) indicate that most of the waters are in equilibrium with ferric oxyhydroxides which range from amorphous material to crystalline goethite (pQ values at 25°C from about 37 to 44, respectively). Stabilities generally increase (higher pQ's) in a given water with time. In general, the lower the dissolved iron, the more soluble is the oxyhydroxide precipitated and the slower its increase in stability. This was observed both in coastal-plain ground waters (pQ = 36.6 − 42.7), and in laboratory aged solutions. The faster the oxidation and hydrolysis rate of dissolved Fe(II), the lower the pQ, as shown by the reaction of mineralized spring waters with varying amounts of surface waters (pQ = 37.2 − 41.5). Where saturation of water with siderite occurs, the siderite is in equilibrium with amorphous ferric oxyhydroxides (pQ = 36.9 − 37.4 for calcium, magnesium bicarbonate ground waters). pQ values > 44.2, in a flooded coal mine, for example, indicate that another iron mineral such as pyrite may control dissolved iron levels.

INTRODUCTION

Contrary to the generally accepted view a significant percentage of the iron in many ground waters (30-70% is not uncommon) is present as suspended ferric oxyhydroxides (see Langmuir and Whittemore, 1971). This is evident from a comparison of iron values in filtered and unfiltered ground-water samples, and preferential complexation and analysis of the dissolved Fe(II) or Fe(III) present, contrasted to the total iron analysis. The occurrence of such suspended iron is not evident from a standard total iron analysis, and has important implications to the water treatment industry. Suspended ferric oxyhydroxides can clog ion exchange treatment units, and if taken as iron, may lead to overdosing with added base during iron removal.

pQ, defined as $pQ = -\log [Fe^{3+}] [OH^-]^3$, where the brackets denote ion activities in solution, is a convenient means of describing the solubility (apparent thermodynamic stability) of ferric oxyhydroxides in equilibrium with water. Studies of the chemistry and mineralogy of precipitated ferric oxyhydroxides indicate that solubilities of the oxyhydroxides vary greatly depending on such factors as dissolved Fe(II), initial precipitation pH, the base used for hydrolysis, surface area of the precipitate, and time (Langmuir and Whittemore, 1971; Whittemore, 1973).

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Limits on pQ are given by the thermodynamic stabilities of specific phases (expressed as pK's) and at 25°C range from 37.1 ± 0.1 for freshly precipitated amorphous material to 44.2 ± 0.3 for coarsely crystalline goethite. These limiting values are used to locate the dissolved iron-ferric oxyhydroxide boundary in an Eh-pH diagram of the system $Fe-H_2O-O_2-CO_2$ (Figure 1) drawn using data from Robie and Waldbaum (1968) for Fe_3O_4 (magnetite), Wagman *et al.* (1969) for Fe^{2+}, Fe^{3+}, and $FeOH^{2+}$, and Langmuir (1969a, 1971, 1972) for the solids $Fe(OH)_2$, $FeCO_3$ (siderite), α-FeOOH (goethite), α-Fe_2O_3 (hematite), and $Fe(OH)_3$ (amorphous material).

Important implications may be drawn from Figure 1. For a given Eh and pH, waters in equilibrium with freshly precipitated amorphous material can contain approximately seven orders of magnitude more dissolved iron than those in equilibrium with coarsely crystalline goethite or hematite. With decreasing solubility of ferric oxyhydroxides, the size of the siderite field is greatly diminished. It would be expected then, that very few ground waters in equilibrium with siderite should be in equilibrium with thermodynamically most stable goethite or hematite. The oxyhydroxides coexisting with siderite in most ground-water systems should be poorly crystalline or of small particle size (large surface area). If siderite were also of small crystal size, its stability field would be further reduced in size. A water in equilibrium with magnetite (Fe_3O_4) could not exist in equilibrium with both siderite and an amorphous or cystalline ferric oxyhydroxide.

Most high-iron ground waters have Eh and pH values on the Fe^{2+}-ferric oxyhydroxide boundary of Figure 1, or at the junction of the Fe^{2+}-$FeCO_3$-ferric oxyhydroxide fields as shown in Barnes and Clarke (1969) and this paper. Acid surface waters, such as an unusually high Fe(III) acid mine drainage in West Virginia (Wilmoth and Hill, 1970), can lie on the Fe^{3+}—or $FeOH^{2+}$—ferric oxyhydroxide boundary. Also, waters high in dissolved sulfur species and of low Eh, such as deep in flooded coal mines, can be on the boundary between Fe^{2+} and FeS_2 stability fields (see Hem, 1961, or Garrels and Christ, 1965, for the stability fields of FeS_2).

Previous workers have used Eh, pH, and Fe(II) measurements as a means of determining which ferric oxyhydroxides are in equilibrium with natural waters (Hem and Cropper, 1959; Back and Barnes, 1965; van Everdingen, 1970; Fayard, 1971; Barnes and Clarke, 1969; Langmuir and Whittemore, 1971). Except for the last two studies, the method

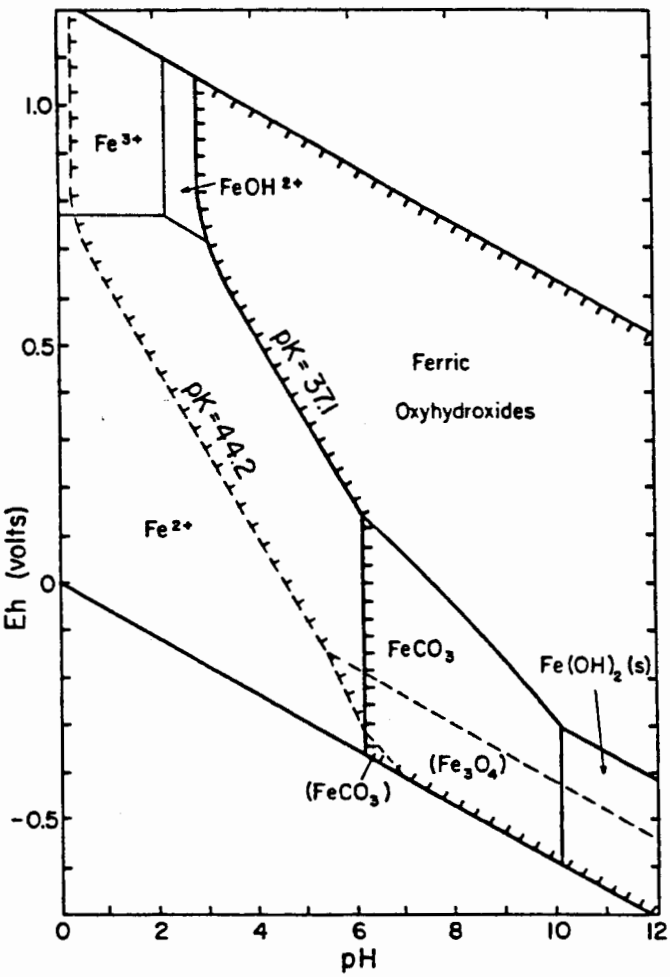

Fig. 1. Eh-pH diagram for the system $Fe-H_2O-O_2-CO_2$. Total dissolved carbonate species equal 10^{-3} M, total dissolved iron species equal 10^{-3} M. Solid species in parentheses are for dashed line fields only.

has generally been to compare measured Eh's with those computed using pH and Fe(II) analyses and equilibrium constants or thermodynamic data for amorphous oxyhydroxide, hematite, and magnetite. In a study of flooded soils Ponnamperuma *et al.* (1967) compared E°'s (standard electrode potentials) computed from their measurements with E°'s calculated from the thermodynamic data of certain oxyhydroxides. Barnes and Clarke (1969) compared ratios of measured ferrous iron activity $[Fe^{2+}]$ to $[Fe^{2+}]$ calculated assuming a particular oxyhydroxide phase.

The activity product pQ is a specific and better measure of the stability of a particular phase or mixture of ferric oxyhydroxide phases in water than is a computed Eh or E°. pQ values in natural waters can be calculated from a knowledge of Eh, pH, Fe(II), and ionic strength using

$$pQ = (E^\circ - Eh)/1.9842 \times 10^{-4}T - \log[Fe^{2+}] - 3(\log K_w + pH) \quad (1)$$

where T is the temperature in K degrees and K_w is the activity product of water (Langmuir and Whittemore, 1971). The largest uncertainties in a calculated pQ result from uncertainties in the measured Eh and pH; field measurements which are typically accurate to ±0.01 volt and ±0.05 pH unit lead to differences of ±0.17 and ±0.15 unit in pQ, respectively. Errors in $[Fe^{2+}]$ as high as ±10% result in differences of only ±0.05 pQ unit. Thus, pQ values calculated from careful analyses of natural waters are probably known with a total uncertainty of ±0.4 unit.

For their better comparison values of pQ were corrected to 25°C using ΔH°_{298} (standard heat of reaction) and ΔC°_{p298} (heat capacity) data for the reactions

$$Fe(OH)_3 = Fe^{3+} + 3OH^- \qquad (2)$$

and

$$\alpha\text{-}FeOOH + H_2O = Fe^{3+} + 3OH^- \qquad (3)$$

Values for the change in pK from 0 to 40°C were calculated from

$$pK_{298} - pK_T = \frac{\Delta H^\circ_{298} + \Delta C^\circ_{p298}(T - 298.15)}{4.5757} \cdot \left[\frac{1}{298.15} - \frac{1}{T}\right] \qquad (4)$$

where ΔH°_{298} = 20.2 ± 0.3 kcal/mol and ΔC°_{p298} = 115 ± 10 cal/deg mol for reaction 2, and ΔH°_{298} = 26.0 ± 0.6 kcal/mol and ΔC°_{p298} = −130.5 ± 2 cal/deg mol for reaction 3. (See Whittemore (1973) for derivation of these values.) Values of $pK_{298} - pK_T$ range from +0.45 to −1.19 units at 35 and 5°C, respectively, for fresh amorphous ferric oxyhydroxides, and from +0.59 to −1.51 units at the same respective temperatures for goethite. These changes represent the range in the correction to 25°C for pK's from 37.1 to 44.2. The correction value applied was interpolated from these limits depending on whether the oxyhydroxide was predominantly amorphous or crystalline; that is, depending on its pQ value. Uncertainties in ΔH°_{298} and ΔC°_{p298} give variations of about ±2% and ±3% in the pK changes at temperature differences of 5° and 25° from 25°C, respectively.

After correction to 25°C, pQ's can be compared to the pK values of ferric oxyhydroxides. A pQ value ≥ 37 and ≤ 44 can indicate oxyhydroxide control on dissolved iron. A pQ < 37 might suggest that the measured Eh is higher than actual (slight aeration possible during sampling or analysis). If the pQ is > 44.2 another iron mineral (such as pyrite) could be controlling the dissolved iron. In the following discussion specific examples of high iron natural water systems have been reevaluated by the application of pQ values (corrected to 25°C) and laboratory results of Whittemore (1973).

EXAMPLES OF pQ VALUES IN HIGH IRON NATURAL WATERS

The pQ approach has been applied previously to a study of ferric oxyhydroxide geochemistry in a coastal-plain ground-water aquifer in New Jersey composed of sands, gravels, and clays (Langmuir and Whittemore, 1971). The presence of suspended ferric oxyhydroxides in the ground water was evident from the difference in iron concentrations in filtered and unfiltered samples and in Fe(II) and Fe(total) values. Calculated pQ values ranged from 38.9 to 42.2 and decreased with increasing pH and decreasing $[Fe^{2+}]$ downdip in the aquifer which contains calcium bicarbonate type waters. Langmuir (1969b) found these waters undersaturated with respect to $FeCO_3$, thus siderite solubility does not limit $[Fe^{2+}]$ levels. The control on pQ, however, appears to be $[Fe^{2+}]$. As the waters move slowly downdip they precipitate out ferric oxyhydroxides which increase in stability more slowly in the presence of decreasing amounts of $[Fe^{2+}]$. This relationship was also observed for sulfate solutions initially 10^{-2} to 10^{-4} M in dissolved ferrous or ferric iron aged in the laboratory (Whittemore, 1973). These solutions also showed that, in general, the lower the initial dissolved iron, the more soluble was the oxyhydroxide precipitated (as shown by smaller pQ's). Thus, moving downdip in the aquifer, as new precipitate formed in the presence of lower $[Fe^{2+}]$ its initial pQ would be smaller.

Langmuir and Whittemore (1971) also showed that pQ values (ranging from 36.6 to 42.7) increased with increasing $[Fe^{2+}]$ in the Maryland ground waters studied by Back and Barnes (1965). These waters were quite undersaturated with siderite. Back and Barnes observed that generally the longer the residence time of the water in parts of the aquifer, the closer the solubility of the oxyhydroxide approached that of hematite. Laboratory aging studies also show generally increasing stabilities (higher pQ's) in a given solution with time. The solutions with $[Fe^{2+}]$ in the same range as the Maryland waters indicate that pQ values > 39 represent ferric oxyhydroxide phases over a year old (Whittemore, 1973).

Fayard (1971) found ground waters in

Table 1. Chemical Data, Saturation Indices, and pQ Values for Louisiana Well Waters Studied by Fayard (1971) (I is molal ionic strength)

Well No.	Temp. (°C)	pH	Eb (volts)	Fe(II) (ppm)	I $\times 10^3$	SI_S^a	SI_S^b	pQ^a at 25°C	pQ^b at 25°C
				Upper Aquifer Unit					
503	20.4	6.91	+0.090	5.7	4.8	+0.26	+0.18	37.2	37.3
505	20.6	7.00	+0.070	7.0	5.1	+0.48	+0.38	37.2	37.3
5[illegible]2	20.6	7.28	+0.053	2.1	5.5	+0.32	+0.16	37.2	37.4
5[illegible]	20.6	7.29	+0.050	4.2	5.1	+0.58	+0.41	36.9	37.1
				Lower Aquifer Unit					
559	20.6	7.27	+0.088	0.83	6.2	−0.05	−0.21	37.0	37.2
510B	20.6	7.26	+0.109	0.75	6.2	−0.10	−0.36	36.7	36.9
518	21.0	7.25	+0.100	0.74	5.9	−0.12	−0.28	36.7	36.9
560	20.8	7.40	+0.090	0.71	6.1	0	−0.22	36.7	36.9
553	20.8	7.22	+0.100	0.74	5.8	−0.17	−0.32	37.0	37.1

[a] Calculated using $K_{FeOH^+} = 10^{-8.30}$
[b] Calculated using $K_{FeOH^+} = 10^{-7.30}$

Louisiana in equilibrium with "ferric hydroxide" from comparisons of measured and calculated Eh's. The calcium, magnesium bicarbonate type waters are located in a confined sandy aquifer separated into an upper and lower unit by a clay layer. Fayard observed limonite, sometimes containing a magnetite core (the probable source of Fe(II) in the waters), occurring as cement in a few clusters of mineral grains. Reevaluating his data in terms of pQ gives 37.0 ± 0.3 for all of the wells (Table 1). This shows that the waters are in apparent equilibrium with freshly precipitated amorphous ferric oxyhydroxide throughout both aquifer units. Fe(III) analyses of 0.00 for all of the samples by Fayard indicated that detectable amounts of suspended oxyhydroxides are not present. Either the precipitate forming adhered to mineral grain surfaces, or O_2 mixing during pumping of the ground water brought the pQ to 37 without time to form precipitate.

Saturation index values of siderite (SI_S) were computed to determine whether the waters are also in equilibrium with siderite (Table 1). $SI_S = \log(Q_S/K_S)$, where K_S is the solubility product of siderite and Q_S is the ion activity product $[Fe^{2+}][CO_3^{2-}]$. When SI_S equals zero the ground water is saturated with respect to siderite. Negative saturation indices indicate undersaturation; positive indices indicate supersaturation. In the lower aquifer unit the waters are saturated with siderite; SI_S values range from 0 to −0.17. In the upper unit the waters are all slightly supersaturated with respect to siderite, which suggests that nucleation of $FeCO_3$ has not yet occurred. If it had, a small particle size effect could be giving the greater siderite solubility. The conclusion drawn based on Figure 1, that the ferric oxyhydroxide phase in equilibrium with siderite most often is amorphous or poorly crystalline, is supported in the above case.

The $FeOH^+$ complex becomes significant (> 1% of total dissolved ferrous iron species Fe(II)) relative to Fe^{2+} at pH's above about 6.3, and is an important factor included in the pQ calculations at the pH's of the above waters. Unfortunately, there is some uncertainty as to the dissociation constant K_{FeOH^+}. Values range from $10^{-5.9}$ to $10^{-9.5}$ (as listed by Bolzan and Arvia, 1963) for several works. In this study we used $K_{FeOH^+} = 10^{-8.30}$ from Leussing and Kolthoff (1953). If K_{FeOH^+} were an order of magnitude larger, the lower unit waters of Fayard's Louisiana aquifer would be slightly undersaturated with siderite, while the pQ values < 37 would be increased to within 0.2 unit of the 37.1 limit for freshly precipitated amorphous oxyhydroxides. These observations show that uncertainty in K_{FeOH^+} is a major source of uncertainty in pQ and SI_S values at pH's > 7.

The dissolved iron in natural waters commonly derives from the oxidation of sulfide minerals, and particularly pyrite as in the following reaction:

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} = 2SO_4^{2-} + 2H^+ \quad (5)$$

One such occurrence is a group of mineral springs called the Paint Pots in British Columbia (van Everdingen, 1970). Ground waters pass through sulfide mineralization, then precipitate bright yellow to reddish-brown deposits of ferric oxyhydroxides where they issue forth as springs. van Everdingen compared four of his measured Eh's with those calculated from pH, Fe(II), and thermodynamic data for assumed iron phases, and found that three computed Eh's were near the Eh's

Table 2. Chemical Data and pQ Values for British Columbia Acid Spring Waters Studied by van Everdingen (1971)

Sample No.	Temp. (°C)	pH	Eh (volts)	Fe(II) (ppm)	I	pQ at 25°C
16	6.7	2.39	+0.578	189	0.0828	41.5
12	10.7	3.70	+0.564	147	0.0486	37.9
20	22.6	3.58	+0.618	47.5	0.0264	37.2
5	23.7	3.48	+0.565	52.1	0.0258	38.3

computed assuming $Fe(OH)_3$ (amorphous) present, and one assuming magnetite present. However, since only ferric oxyhydroxide minerals were observed in the spring deposits he also assigned the latter value to $Fe(OH)_3$ precipitation. His data recalculated as pQ values are listed in Table 2. Samples 16 and 12 were from spring sources. Spring 16 waters may be in equilibrium with a crystalline phase, while spring 12 waters have a pQ much closer to that of amorphous oxyhydroxides. A higher temperature and pH, and the observation that fresh water enters nearby pools as seeps suggests that surface waters could be acting to oxidize and hydrolyze iron at a faster rate in spring 12 than in spring 16. The spring waters then join a small [illegible]-water creek and actively precipitate amorphous material as shown by pQ = 37.2 in sample 20. At the point before discharging into a river (sample 5) the pQ increases slightly suggesting a slower rate of precipitation or an aging of the oxyhydroxides which have formed poorly crystalline material.

Natural waters very high in dissolved iron (> 100 ppm Fe(II)) and SO_4^{2-}, and of low pH, commonly drain from strip and underground coal mines. Analyses of such waters in flooded anthracite coal mines in northeastern Pennsylvania by Barnes *et al.* (1964) were reevaluated by comparing computed pQ values with their observations. As an example, in the Loree No. 2 shaft, (Table 3) the waters down to 233 feet depth could be undersaturated with respect to less stable ferric oxyhydroxides or could be in equilibrium with well crystallized phases. If the latter case is true, the high Fe(II) present probably accelerates crystallization. From 292 to 579 feet the pQ's are low (38.2 ± 0.1) indicating relatively rapid precipitation of poorly crystalline oxyhydroxides. This is confirmed by the presence of yellow turbidity in the waters. The higher Eh and lower pQ suggest that fresh, oxygenated ground waters may be entering the mine in this section, causing iron oxidation and hydrolysis. At the deepest levels of the shaft the pQ's are higher than could be in equilibrium with any ferric oxyhydroxide phase. They plot in the FeS_2 field of the Eh-pH diagram of the Fe-H_2O-O_2-S system given by Barnes *et al.* (1964) and were observed to have an H_2S odor. Thus, the dissolved iron is probably controlled at these depths by FeS_2 solubility.

In comparison with the flooded anthracite mines, a flooded bituminous coal mine water in Hollywood, Pennsylvania analyzed in this study (Table 4) gives intermediate pQ's implying equilibrium with poorly crystalline ferric oxyhydroxides. As it issued from a filled borehole, the water was perfectly clear. The change in dissolved Fe(II) and pQ over the two-month interval between the samples suggests a slight but significant change in the hydrologic system.

Observations in this study may be applied to the treatment of high iron waters. Amorphous or poorly crystalline ferric oxyhydroxide precipitates contain more water and generally

Table 3. Chemical Data and pQ Values for Pennsylvania Flooded Anthracite Mine Waters Studied by Barnes *et al.* (1964)

Sample Depth (feet)	Temp. (°C)	pH	Eh (volts)	Fe(II) (ppm)	I	pQ at 25°C	Color of Water
224	14	3.41	+0.322	34	0.050	43.4	Clear
233	14	3.40	+0.312	34	0.050	43.6	Clear
292	17	3.55	+0.533	478	0.140	38.2	Yellow turbidity
438	17	3.51	+0.533	488	0.145	38.3	Yellow turbidity
467	17	3.56	+0.568	488	0.154	38.2	Yellow turbidity
579	17.5	3.40	+0.562	546	0.168	38.1	Yellow turbidity
751	17	4.00	−0.025	1073	0.244	46.2	Clear
808	17	3.92	−0.103	1463	0.282	48.6	Clear

Table 4. Chemical Data and pQ Values for a Flooded Bituminous Coal Mine Water, Hollywood, Pennsylvania

Sample Date	*Temp. (°C)*	*pH*	*Eh (volts)*	*Fe(II) (ppm)*	*I*	*pQ at 25°C*
8-5-69	11.3	3.13	+0.583	670	0.13	38.7
10-7-69	11.2	3.15	+0.547	723	0.13	39.2

settle more slowly than the denser crystalline phases. Thus, slower oxidation and hydrolysis of Fe(II) as in the neutralization of acid mine drainage with limestone would be expected to produce a denser and faster settling precipitate than that formed during lime addition. This has been confirmed by Holland (1970) and Lovell (1970). Also, recycling oxyhydroxide sludge back into untreated water could allow the precipitate to become more crystalline and of larger particle size in the presence of high dissolved iron.

CONCLUSION

The activity product pQ is a specific value which can be used to describe the apparent thermodynamic stability of ferric oxyhydroxide phases in equilibrium with natural waters whether these phases are in suspension or in a sediment. Coupled with other geochemical data pQ values can suggest whether a system is actively precipitating amorphous or poorly crystalline ferric oxyhydroxides (pQ's near 37) or in equilibrium with or dissolving more stable oxyhydroxides (pQ's 39 to 44). In general, the faster the oxidation and hydrolysis rate and the smaller the concentration of Fe(II), the lower is the pQ value of the oxyhydroxides precipitated. Where saturation of water with siderite occurs, the siderite is most likely in equilibrium with amorphous ferric oxyhydroxides. The control on dissolved iron in waters for which pQ's are > 44.2 may be by another mineral, probably most commonly pyrite or other iron sulfides.

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