Evolution of the reactive surface area of ferrihydrite: Time, pH, and temperature dependency of growth by Ostwald ripening

Electronic Supplementary Information

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Flow chamber design

Fig. S1 Experimental setup for mixing a Fe nitrate and Na hydroxide solution added with motor burets. The tips, where mixing occurs, is mounted about halfway on a pH electrode hanging in a vessel that is kept under N₂ atmosphere. This allows continuous pH-recording of the mixed solution, passing the glass membrane before it flows into the vessel where it is stirred magnetically. The pH-recording allows the setting of the rate of the NaOH addition at a constant rate (8 mL min⁻¹) of the Fe nitrate addition, keeping the pH value about 0.5-1.0 pH unit below the final target value. Progressively, the vessel gets filled and the recorded pH then refers to the suspension as a whole that is subsequently increased to the final pH once the addition of partially neutralized Fe-nitrate solution has stopped (~3 minutes). The final NaOH addition to reach the target pH value is done at a lower speed.
Size-dependent Stern layer capacitances and adsorption

Primary charge

The capacitance of a spherical capacitor \( C_{1,r} \) can be given as:

\[
C_{1,r} = \frac{r + \Delta r}{r} C_1
\]

in which \( r \) is the inner radius of the sphere and \( \Delta r \) the thickness of the layer.

In case of an Extended Stern (ES) layer model (Hiemstra and Van Riemsdijk 2006) with two Stern layers, a value of \( \Delta r_1 = 0.35 \) nm is used to calculate the inner Stern layer capacitance from \( C_1 \) of a flat layer at a given particle radius \( r \).

The capacitance of the second spherical Stern layer \( C_{2,r} \) is found with:

\[
C_{2,r} = \frac{r + \Delta r_1 + \Delta r_2}{r + \Delta r_1} C_2
\]

using \( \Delta r_2 = 0.35 \) nm as derived for the compact double layer with a total thickness of 0.7 nm, equivalent with the packed size of nearly three water molecules (Hiemstra and Van Riemsdijk 2006). In the calculation, \( C_2 \) is the capacitance of the outer Stern layer of a flat layer.

For Fh, the Stern layer capacitance values for the flat layer \((r \to \infty)\) have been set equal to the numbers found for well-crystallized goethite, i.e. \( C_1 = 0.9 \) F m\(^{-2}\) and \( C_2 = 0.74 \) F m\(^{-2}\) (Hiemstra and Van Riemsdijk 2006). For 2LFh, the typical capacitance values with a diameter of \( \sim 2.5 \) nm are \( C_1 = 1.15 \) F m\(^{-2}\) and \( C_2 = 0.90 \) F m\(^{-2}\) (Hiemstra and Zhao 2016). These values are very different from the values given by Antelo et al. (2010, 2015), i.e. \( C_1 = 0.74 \) F m\(^{-2}\) and \( C_2 = 0.93 \) F m\(^{-2}\). The much lower value for \( C_1 \) indicates a lower surface charge density.
**Phosphate adsorption and curvature**

The effect of the surface curvature on the PO\textsubscript{4} adsorption at a given pH and PO\textsubscript{4} equilibrium concentration is shown in Fig.S2 (left panel). At decrease of the particle size, the electrostatic effects decrease. The reduction of the field strength allows the adsorption of more ions. The field becomes less limiting.

In case of a constant PO\textsubscript{4} loading (right panel), the increase of the capacitance at decrease of the particle size will lead to a lower equilibrium concentration of phosphate.

![Graph showing phosphate adsorption and curvature](image)

Fig. S2 Left panel. Adsorption of phosphate as a function of particle size, in case of spherical Stern layers (ES model) for Fh at the conditions given. The adsorption increases by ~10% or less compared to the adsorption at a flat surface. A similar size dependency of the adsorption due to a variable capacity has been illustrated in Hiemstra and Zhao (2016). Right panel. Logarithm of the equilibrium concentration of PO\textsubscript{4} at a constant surface loading (1 and 2 µmol PO\textsubscript{4} m\textsuperscript{-2} at respectively pH=8 and pH=5 in 0.01 M NaNO\textsubscript{3}). The equilibrium concentration decreases substantially.
Deriving the rate of growth $R$ (mol m$^{-2}$ h$^{-1}$)

Time-dependency of the particle size

For obtaining the experimental rate of growth $R$, the function:

$$d = kt^{1/n} + d_0$$  \hfill (EA-3)

has been used in the data analysis (Fig. S3) Equation EA-3 is a general equation for describing the growth of particles with different theories and mechanisms (Huang, Zhang et al. 2003). The value of exponent $n$ depends on the rate limitation and conditions assumed. At crystal growth controlled by diffusion of ions across the solid-solution interface, $n$ is equal to the value $n = 3$. In that case, the volume ($V \propto d^3$) increases linearly with the ageing time $t$ as derived by Lifshitz and Slyozov (1961), and Wagner (1961). However, our data for ageing of Fh in a NaNO$_3$ solution show a non-linear relation of the volume $V$ with time. For Fh, the process of growth has another time dependency. The growth decrease more quickly with time.

Fig. S3. Particle diameter ($d$) related to a power function of time ($t^{1/n}$) for ageing at pH 5 and 9. For each pH, the best value of the exponent $1/n$ of the time (h) is optimized to get the best description with a linear function $d = k t^{1/n} + d_0$, in which $d_0$ is the diameter at $t = 0$.

In the pH range 5-9, the fitted value of exponent $1/n$ equals $0.21 \pm 0.06$ if the value of $d_0$ is simultaneously fitted. The value $d_0$ represents the initial size at $t = 0$. It is the intercept in
the plot. If a common value of $d_o$ is assumed ($d_o = 1.68$ nm), $1/n = 0.26 \pm 0.05$. In the latter case, the corresponding inverse value is $n = 3.9 \pm 0.7$.

Rate of growth
With the above function (EA-3), the rate of growth $R$ has been derived by fitting the values $k$, $d_o$, and $1/n$ for each data set (Fig.S3). The calculation of $R$ starts by taking numerically the derivatives of the optimized function at a chosen time $t$. The procedure requires simultaneously the calculation of the mass density $\rho_{nano}$ according to (Hiemstra 2018b):

$$\rho_{nano} = \frac{M_{core}}{n_O V_O} - \left( \frac{M_{core}}{n_O} - M_{H_2O} \right) \frac{6}{d} N_{H_2O}$$  \hspace{1cm} (EA - 4)

and specific surface area $A$ according to:

$$A = \frac{6}{\rho_{nano} d}$$  \hspace{1cm} (EA - 5)

followed by calculating the molar mass $M_{nano}$ according to:

$$M_{nano} = M_{core} \frac{1}{\left( 1 - A N_{H_2O} M_{H_2O} \right)}$$  \hspace{1cm} (EA - 6)

In combination ($\rho_{nano}$, $M_{nano}$), one can obtain the corresponding number of Fe per particle ($n_{Fe}$), according to:

$$n_{Fe} = \frac{\rho_{nano}}{M_{nano}} \frac{\pi d^3}{6} N_A$$  \hspace{1cm} (EA - 7)

In the above equations, $N_{H2O}$ is the surface density of coordinated water ($12.6 \times 10^6$ mol m$^{-2}$ (Hiemstra 2015)), $n_O$ is the amount of oxygen per Fe in the bulk (1.6), $M_{core}$ is the molar mass of the Fh core (81.65 g mol$^{-1}$), $M_{H2O}$ is the molar mass of water (18 g mol$^{-1}$), and $N_A$ is Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$).

In equation EA-4, $V_O$ is the lattice volume, expressed per mol oxygen. The value of $V_O$ can be estimated from the relation between mass density (g m$^{-3}$) and molar mass per oxygen...
(g / mol O) (Hiemstra and Van Riemsdijk 2009a) or alternatively, it can be calculated from the chemical composition combined with the volume of the unit cell that provides the mass density of the bulk (Hiemstra 2018a):

\[
V_O = \frac{M_{\text{core}}}{n_O \rho_{\text{core}}} \quad (EA - 8)
\]

For iron (hydr) oxides in general, \(V_O \sim 10.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ O} \) (Hiemstra and Van Riemsdijk 2009a). Based on the unit cell dimensions derived by Wang et al. (2016) and Pinney et al. (2009), \(V_O = 10.7 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ O} \). The number is equivalent with a mass density of \(\rho_{\text{core}} = 4.77 \times 10^6 \text{ g m}^{-3}\), but might be slightly higher (~ 2 %) according to other parametrizations (Harrington, Hausner et al. 2010, Michel, Barron et al. 2010, Maillot, Morin et al. 2011) leading to \(\rho_{\text{core}} = 4.92 \pm 0.03 \times 10^6 \text{ g m}^{-3}\) and \(V_O = 10.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ O}\).

Ultimately, the rate of growth \(R\) (mol m\(^{-2}\) h\(^{-1}\)) follows from the change of \(n_{\text{Fe}}\) with change of time \(t\), scaled to the surface area of the particle \(A_\# = \pi d^2\) at the corresponding time, according to:

\[
R = \frac{dn_{\text{Fe}}}{dt} \frac{1}{A_\#} \quad (EA - 9)
\]
A monolayer of Fe: surface density

Fig. S4 Mean surface density of Fe (spheres) at the repetitive growth of Fh using the a-direction of the unit cell with \( a = 0.587 \) nm as measure for the representative distance (Harrington, Hausner et al. 2011). The surface density has been derived by step-wise increasing the particle diameter \( d \) with the repetitive Fe-Fe distance \( (L = \frac{1}{2}\sqrt{3} \frac{a}{2} = 0.25 \) nm), i.e. \( d + 2L \), and calculate self-consistently with the equations given in the main text the increase of the amount of Fe in the volume of the layer with thickness \( L \). By scaling to the corresponding particle surface area \( A_\theta = \pi d^2 \), the Fe surface density follows. Another approach is to use the mean Fe-Fe distance in the Fh lattice as repetitive distance \( (L = 0.33 \pm 0.02 \) nm), leading to a higher surface density (squares). If individual crystal faces are considered, similar values are found for the mean repetitive growth, i.e. \( \sim 15 \) \( \mu \)mol m\(^{-2}\) for the 100 or 010 face, and \( \sim 20 \) \( \mu \)mol m\(^{-2}\) for the 001 face.

The orange color gives the size of 6LFh (~ 5.5 nm, n_Fe ~ 2600), formed by forced hydrolysis of Fe(III) at 75 °C (Guyodo, Banerjee et al. 2006)(Gentile, Wang et al. 2018). If formed by Fe adsorption to Fe\(_{13}\) nuclei, the formation of this 6LFH particle is equivalent with the binding of \( \sim 6-8 \) monolayers of Fe.
Fig. S5. A ferrihydrite particle built from 45 Fe polyhedra with the composition \( \text{Fe}_{45}\text{O}_{132}\text{H}_{129} \). This is equivalent to \( \text{FeO}_{1.4}(\text{OH})_{0.2}\text{nH}_2\text{O} \) with \( n = 1.5 \). The blue spheres are oxygen ions. The protons are not shown. The particle has a \( \text{Fe}_{13} \) signature and contains two linked \( \text{Fe}_{13} \) units that are given with red, dark red, and orange-colored polyhedra. Additionally attached Fe polyhedra are given in blue. The constructed particle is surface depleted (Hiemstra 2013) by \( \text{Fe}_2 \) (orange) octahedra and \( \text{Fe}_3 \) (dark red) tetrahedra because these polyhedra are considered as less stable at the surface of Fh when forming singly coordinated surface groups.
Influence of initial particle size on ageing

Fig. S6. Time dependency of the mean particle diameter \( d \) (nm), number of Fe per particle \( n_{Fe} \), specific surface area \( A \) (m\(^2\) g\(^{-1}\)), and rate of growth \( R \) (\( \mu \)mol m\(^{-2}\) h\(^{-1}\)) of traditionally synthesized Fh, produced and aged at pH 8.2 in 0.01 M NaNO\(_3\) at 20 °C (spheres) for \( t \geq 4 \) hours. The lines have been calculated with the dynamic model for \( \log k = -4.97 \) (eq.8, main text) using different values for the amount of Fe present in the initial particles.

The model results of Fig. S6 show that increase of the size of the initial particles (\( n_{Fe} \)) does not lead to a considerable increase of the particle size at prolonged ageing. The reason is that the increase of the particle size leads to a substantial decrease of the solubility and supersaturation, acting as a very strong negative feedback on the rate of growth \( R \). However, the choice of the value of \( n_{Fe} \) at time \( t = 0 \) becomes critical at shorter times of ageing as used in the experiment with the organic pH buffers (\( t = 0.1 \) and 1.5 hours). The dotted vertical line indicates 4 hours of ageing.
Rate limitation by diffusion across the solid-water interface

The rate limitation of growth by diffusion from the solution to the surface leads to a time dependent growth of the diameter according to $\Delta d = k t^{1/n}$ with $n = 3$, according to Lifshitz and Slyozov (1961). This theory is based on combining Fick first law with the Ostwald-Freundlich equation for describing the solubility as a function of the particle size. The latter equation is used in its linearized form.

The classical Ostwald-Freundlich (OF) equation can be given as:

$$RT \ln \frac{Q_{so}}{K_{so}} = \frac{2}{3} \gamma A_c = \frac{M_{\text{nano}} 2\gamma}{\rho_{\text{nano}} r_c} \quad (EA-10)$$

in which $Q_{so}$ and $K_{so}$ are respectively the solubility products of the actual Fh of given radius of the critical particles and the virtual bulk, and $A_c$ is the specific surface area ($m^2 \text{ mol}^{-1}$) of the critical particle in the size distribution.

Taking the exponential of equation $EA-10$ and simplifying with $e^x = 1 + x$ for $x \rightarrow 0$, one gets the linearized Ostwald-Freundlich (L-OF) equation:

$$\frac{Q_{so}}{K_{so}} = e^{\frac{1}{RT} \frac{M_{\text{nano}} 2\gamma}{\rho_{\text{nano}} r_c}} \approx 1 + \frac{2 \gamma M_{\text{nano}}}{RT \rho_{\text{nano}} r_c} \quad (EA-11)$$

With increase of the critical radius $r_c$, linearization of the equation is increasingly justified as shown in Fig. S7. In Fig. S7, we have given the difference in super saturation. Only at a large size, the relative difference in the calculated solution concentration of OF and L-OF becomes small. For $d \sim 6.5$ nm, $\Delta(Q_{so}/K_{so}) = 1$ as indicated in the graph with the black sphere. In that case, $Q_{so}/K_{so}$ (OF) $\sim 3$ and $Q_{so}/K_{so}$ (L-OF) $\sim 2$, i.e. the super saturation calculated with the OF approach is 50% higher. The difference quickly increases at a smaller particle size.
Fig. S7 Size-dependent difference in relative solution concentration ($\Delta Q_{so}$) of Fh calculated with the classical and the linearized Ostwald-Freundlich equation scaled to the solubility of the virtual bulk of Fh ($K_{so}$). The calculated concentration difference is orders of magnitude different when particles are small. The black sphere locates the system in which the relative difference has decreased to $\Delta(Q_{so}/K_{so})= 1$, where the super saturation calculated by the OF equation is 50% higher than with the L-OF approach.

The factors $Q_{so}$ and $K_{so}$ can be linked to the concentration of dissolved aqueous species (aq) at a given pH in equilibrium with respectively a particle of critical size ($c_{rc}$) and virtual bulk material at infinite size $c_{\infty}$, leading to:

$$c_{rc} = c_{\infty} + \frac{2 \gamma \rho_{nano}}{RT \rho_{nano}} \frac{1}{r_c} c_{\infty} \equiv c_{\infty} + \frac{\alpha}{r_c}$$  \hspace{1cm} (EA – 12)

By defining super saturation of the solution as $\Delta \equiv c_o - c_{\infty}$ in which $c_o$ is actual solution, Lifshitz and Slyozov(1961) derived for the concentration gradient between solution and surface of the growing particles with radius $r$

$$c_{rc} - c_o = \left(\frac{\alpha}{r_c} + c_{\infty}\right) - (\Delta - c_{\infty}) = \frac{\alpha}{r_c} + \Delta$$ \hspace{1cm} (EA – 13)

This concentration difference is introduced in the Fick’s first law of diffusion.
**Required length of diffusion explaining the rate of growth of Fh**

Our measured rates of growth ($R$) are typically in the order of $R \sim 0.01 - 10 \, \mu\text{mol m}^{-2} \, \text{h}^{-1}$ or $R \sim 3 \times 10^{-12} - 3 \times 10^{-9} \, \text{mol m}^{-2} \, \text{s}^{-1}$. Assuming that the rate of growth is limited by diffusion across the solid-solution interface, one may calculate the diffusion length required to explain the experimental rate of growth $R$ by using Fick’s first law as a first approach that is combined with the classical Ostwald Freundlich equation.

According to Fick’s first law, we may write for the flux $F$ (mol s$^{-1}$):

$$F = -DA_# \frac{dc}{dx}$$  \hspace{1cm} (EA – 14)

in which $D$ is the diffusion coefficient in m$^2$ s$^{-1}$, $A_#$ is the surface area (m$^2$), and $\frac{dc}{dx}$ is the linear concentration gradient with the concentration $c$ in mol m$^{-3}$ and the diffusion length $x$ in m.

Rewriting of $EA$-14 leads to an expression for the length of the diffusion path $L$ between the solution ($x = 0$) and surface ($x = x$):

$$L = \frac{1}{F/A_#} D (c_o - c_{surf}) \sim \frac{D}{R} c_{eq}$$  \hspace{1cm} (EA-15)

in which the flux $F$ per unit surface area $A_#$ represents the rate $R$ of growth ($R = F/A_#$ in mol m$^{-2}$ s$^{-1}$). The concentration in the solution ($c_o$) is determined by the solubility of the critical particle with size $d_{crit}$ and the concentration at the surface ($c_{surf}$) is determined by that of Fh particle of mean size $d_{mean}$. For a polydisperse Fh suspension, both sizes are related by a factor of about $\phi = d_{mean} / d_{crit} = 3/2$. The corresponding equilibrium concentrations can be calculated with the Ostwald-Freundlich equation. If the difference $c_o - c_{surf}$ is relatively large, one may simplify to $c_o - c_{surf} = c_{eq}$ in which the latter is the equilibrium concentration maintained by the critical particles.

In Fig. S8, the distance $L$ at which the rate is limited by diffusion is given. It has been calculated for a suspension with Fh particles of different mean size having a rate of growth in the range $R = 0.01 - 10 \, \mu\text{mol m}^{-2} \, \text{h}^{-1}$ or $\sim 3 - 300 \times 10^{-12} \, \text{mol m}^{-2} \, \text{s}^{-1}$, taken from Fig.4 in the main text. The corresponding size dependent solubility products ($\log Q_{so} = \log(\text{Fe}^{3+}) + 3 \log(\text{OH}^-)$) can be used to calculate the solution concentrations as a function of pH.
on the size, the concentrations at neutral pH are in the order of about $10^{-7}$ - $10^{-9}$ M or $10^{-4}$ - $10^{-6}$ mol m$^{-3}$.

![Image](image.png)

**Fig. S8.** Interfacial length of diffusion $L$ (µm) that can explain the observed rates of growth ($R$) of Fh with mean sizes ($d_{\text{mean}}$ in nm) as given. Compared to the mean particle size of Fh (~nm), the diffusion length $L$ (~ µm) is very large, making rate limitation by interfacial transport unlikely, particularly because the Fh particles in the actual suspension are aggregated. The Fh solubility has been calculated with the Ostwald-Freundlich equation (eq.7 main text) using a surface Gibbs free energy of 0.186 J m$^{-2}$, a size distribution ratio of $\phi = d_{\text{mean}} / d_{\text{crit}} = 3/2$, and a solubility product for Fh bulk of log$K_{s\text{o}} = -40.6$. The rates (µmol m$^{-2}$ h$^{-1}$) used to calculate $L$ are 10 (blue spheres), 1.0 (red triangles), 0.1 (green diamonds), and 0.01 (yellow squares), typically for a timescale of ageing being respectively about 0.1, 1, 10, and 100 h.

Using a representative value for the diffusion coefficient, for instance $D = 0.6 \times 10^{-9}$ m$^2$ s$^{-1}$ for Fe$^{3+}$, the calculated distance $L$ (Fig. S8) at which the rate becomes limited by diffusion is typically in the order around one µm, depending on the particle size and pH in solution (Fig. S8). As these distances are relatively large compared to the size of the Fh nanoparticle (> 100-1000 times), the calculated result supports our interpretation that the rate of growth is not limited by diffusion across the solid-solution interface but by another process. Moreover, Fig. S8 shows that if diffusion would be rate-controlling, the diffusion length would not change with size or time, whereas our data would point to a significant change (Fig. S8).
Mean particle-particle distance in suspensions

One may calculate the mean equivalent distance $x$ (m) between Fh particles in a suspension in the case of a homogenous distribution over space (no aggregation), taking the one-dimensional distance of the Fh particle density in the suspension according to:

$$x = \left( \frac{n_{Fe} M_{nano}}{N_{av} \rho_{sus}} \right)^{1/3}$$  \hspace{1cm} (EA-16)

in which $n_{Fe}$ is the number of Fe per particle and $N_{av}$ is Avogadro’s number (mol$^{-1}$), $M_{nano}$ is the molar mass of Fh (g Fh mol$^{-1}$ Fe), and $\rho_{sus}$ is the suspension concentration (g m$^{-3}$). In combination, this gives the Fh particle density (Fh particles m$^{-3}$). The third root of this particle density can be seen as representative for the mean particle distance $x$ (m). The calculated mean distance for representative particles of certain size ($d$-Fh) is given in the table below.

| $d$-Fh (nm) | $M_{nano}$ (g mol$^{-1}$) | $n_{Fe}$ | $x$ (nm) |
|-------------|---------------------------|---------|---------|
| 1.7         | 108                       | 47      | 20      |
| 2.0         | 101                       | 88      | 25      |
| 2.5         | 95                        | 195     | 31      |
| 3.0         | 92                        | 363     | 38      |
| 5           | 87                        | 1930    | 65      |
| 10          | 84                        | 16930   | 133     |

Collectively, the above shows that rate limitation by diffusion across the interface cannot explain the rate of growth of Fh. The growth of Fh is much slower. In literature, rates of growth of materials are often limited by diffusion. This will occur if the reaction at the surface is fast, creating relatively large particles and low super saturation, i.e. low concentration gradient.

Finally, it is interesting to note that the rate of Fe attachment is rather comparable with the rate of the adsorption of ions such as PO$_4$, being typically in the order of the scale of µmol m$^{-2}$ h$^{-1}$. 
Ageing of 6LFh

Fig. S9. Time dependency of the mean particle diameter $d$ (nm), and specific surface area $A$ (m$^2$ g$^{-1}$) of 6LFh. If synthesized by forced hydrolysis at 75 °C for 10-12 minutes, according to the method of Schwertmann and Cornell (1991), the initial size is about 5.5 nm (Guyodo, Banerjee et al. 2006, Gentile, Wang et al. 2018). According to our model (lines), storage and long-term ageing of the material at 20 °C leads to no notable change in size and surface area by Ostwald ripening, in agreement with recent data collected by SAXS (Gentile, Wang et al. 2018) after 1 and 9 months of ageing. At 75 °C, some classical Ostwald ripening may occur according to our model, but more significant changes may be expected from oriented particle attachment and/or fusion, which is typical for ageing at high temperature (Burleson and Penn 2006).
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