



Effect of silicic acid on aggregation of hydrous ferric oxide

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ABSTRACT

Colloidal properties of hydrous ferric oxide (HFO) have received much attention due to their environmental relevance. In this study, aggregation of HFO was determined by time-resolved dynamic light scattering and test tube experiments, evaluating surface charge via zeta potential (ζ) measurements. The silicic acid charge varies with protonation and deprotonation at different pH levels. As an adsorbing species, silicic acid could modify surface charge and affect the colloidal stability of HFO. Electrophoretic experiments revealed that silicic acid lowered particle ζ , decreased the isoelectric point (iep), and allowed HFO to aggregate at a lower pH. Reversal of charge was observed at pH 7.5, 7.0, 6.4, and 6.2 for silicic acid concentrations of 0, 0.5, 1.0 and 1.5 mM, respectively. By demonstrating that silicic acid shifts the iep of HFO to lower pH values, results indicate that silicic acid can change the aggregation properties of HFO. Both light scattering and test tube experiments revealed a “peak aggregation” at pH 5.5-7.5 in the presence of silicic acid. As this pH range is typical for many aqueous systems and soils, we conclude that silicic acid likely plays an important role in HFO transport in water and accumulation of particulate HFO in soil horizons.

Keywords: Silicic acid, hydrous ferric oxide, surface charge, aggregation.

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1. Introduction

Hydrous ferric oxides (HFO) are poorly crystalline forms of Fe(III) that are often found in various natural environments including marine systems and soils (Towe and Bradley, 1967; Combes et al., 1989; Cornell and Schwertmann, 1996; Spadini et al., 2003). These minerals can be formed as initial products of precipitation from oxygenated,

Fe-rich, aqueous solutions, or by bacteria, either as a result of a metabolic activity or passive adsorption of dissolved Fe, followed by nucleation reactions (Fortin and Langley, 2005). In an aqueous solution, HFO is hydrated, and Fe-OH groups become chemically reactive. The charge on the HFO's surface, established by protonation or deprotonation of the Fe-OH groups, depends on pH of the solution (Cornell and Schwertmann, 1996; Davis et al., 2002; Li et al., 2016). The nature and the extent of the

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charge is a known factor governing the colloidal properties of HFO. The isoelectric point (iep), characterized as the pH at which the positive and negative charges of a given compound are equal, has been widely used to describe the aggregation properties of Fe oxides in general, and HFO in particular. HFO is expected to coagulate at pH levels near its iep, even at low ionic strengths, and to disperse at pH levels distant from the iep (Cornell and Schwertmann, 1996). Numerous studies state that HFO surface adsorption of anions or dissolved organic matter from its surrounding solution might lead to a decrease of the HFO iep, modifying aggregation properties. However, the effect of silicic acid, one of the most common solutes in the soil solution, has not yet been reported.

In nature, silicic acid is often found in monomeric form ($\text{Si}(\text{OH})_4$), which can be either protonated or deprotonated, and can also condense to a variable extent, potentially yielding many dissolved species of polymeric silicic acids (Iler, 1979; Dove and Rimstidt, 1994) and nanocolloidal silica (Icopini et al., 2005) coexisting in equilibrium. The prevalence of each of these species, as well as their degree of protonation or deprotonation and resultant charge, depends primarily on pH, but is also influenced by other factors such as ionic strength (Icopini et al., 2005) and temperature (Rothbaum and Rohde, 1979). The monomer is found in most natural waters (Dove, 1995; Dietzel, 2000). In soils, silicic acid can be found in both monomeric and polymeric forms (Wonisch et al., 2008). Concentrations can reach up to 1.99 mM (Karathanasis, 2002), but are more commonly observed from ca 0.1 to 0.6 mM (Epstein, 2001; Sommer et al., 2006). Silicic acid fluxes could presumably affect soil stability and co-transport of contaminants with HFO by changing HFO colloidal properties.

Earlier research has applied time-resolved dynamic light scattering (DLS), which

quantifies the hydrodynamic diameter of particles in suspension, to monodisperse model colloids such as latex microspheres (Holthoff et al., 1996) and clay colloids (Kretzschmar et al., 1998; Mori et al., 2001). As reported by Cornell and Schwertmann (1996) and Pike and Abbiss (1997), this method can also be effective with large particles possessing a non-spherical shape.

In this study, a synthesized HFO sample was used for characterization of aggregation under the effect of silicic acid. DLS and test tube experiments were combined to examine particle size evolution and aggregation kinetics of HFO under the effect of silicic acid as functions of pH. Because particle surface charge is the most important parameter for aggregation, zeta potentials (ζ) were investigated to examine the effect of adsorption of silicic acid on surface charge properties and its correlation with the colloidal stability of HFO.

2. Materials and methods

2.1. Materials

An amount of 68 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ from Sigma (USA) was dissolved in 600 mL of sterile deionized water. Sterile 5 M NaOH was added dropwise to the ferric chloride solution until the pH of the HFO suspension was stable at pH 7. The HFO suspension was poured into centrifuge bottles and centrifuged at 4°C for 20 min, after which the supernatant was poured off and discarded. The HFO precipitates were washed 3 times with autoclaved water. HFO precipitates were re-suspended in 500 mL autoclaved deionized water to make an HFO suspension at the concentration of 1 mg mL⁻¹. Transmission electron microscopy images, captured using a JEOL 1010 TEM (USA), revealed aggregates of uniform HFO nanoparticles with an approximate elementary particle diameter of 10 nm (Figure 1).

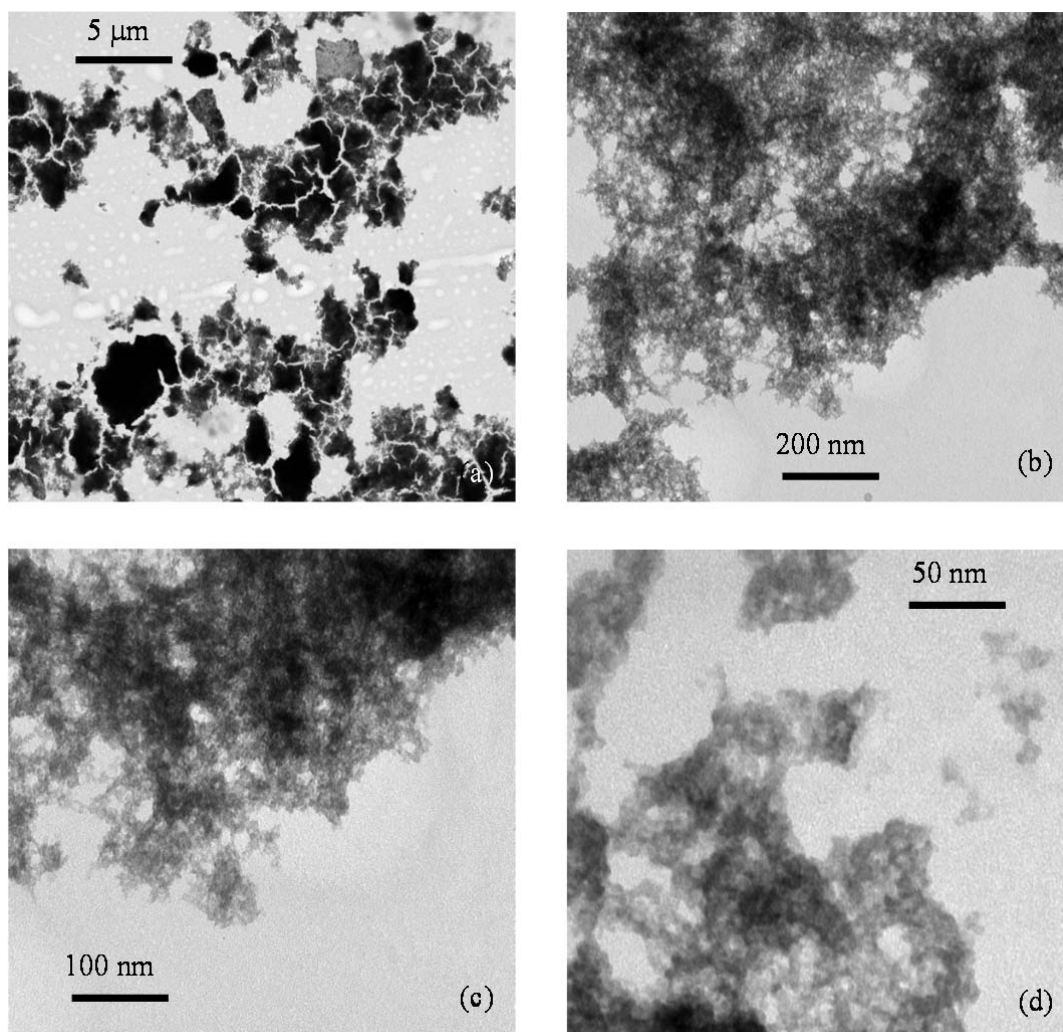


Figure 1. TEM image showing particles/clusters of HFO at different magnifications: (a) 1:2000, (b) 1:50,000; (c) 1:100,000 and (d) 1:200,000

Solutions for the evaluation of silicic acid effects were prepared by dissolving 20 g of pure silica gel with a particle size of 0.15 μm (Fisher Scientific Company, USA) in 200 mL deionized water by stirring at 70°C for 3 d. The obtained bulk solution was kept for one week at room temperature and passed through a 0.45 μm pore-size cellulose acetate filter. Si in the resultant filtrate was quantified by the molybdate blue method with a UV-Vis

spectrophotometer (L-VIS-400, Labnics Company, USA), and then diluted to 2.0 mM.

2.2. Methods

2.2.1. Zeta potential measurements

The ζ for silicic acid and its mixtures with HFO as functions of pH and ionic strength were determined. As silicic acid may partially occur in polymeric forms with nano-sized

particles, the ζ of the particulates can be measured using a combination of laser Doppler velocimetry and phase analysis light scattering (Hunter, 1981). The ζ of silicic acid was examined at silicic acid concentrations of 0.5, 1.0, and 1.5 mM over a pH range of ~ 2 to ~ 12 . The pH of these solutions was adjusted to targeted values by dropwise addition of either 0.5 M HCl or 0.5 M NaOH solution. Each 1 mL of the NaCl solution was mixed with 2.5, 5.0, and 7.5 mL of 2 mM silicic acid suspension (prepared as described above) and filled with deionized water to a final volume of 10 mL. Final silicic acid concentrations of the obtained suspensions were 0.5, 1.0, and 1.5 mM. A subsample of 1.0 mL was then directly transferred into a DTS1070-folded capillary cell. ζ was measured in triplicate using a Malvern Zetasizer Nano ZS (UK).

In experiments measuring the ζ of the HFO suspensions as a function of pH, ζ was determined at silicic acid concentrations of 0, 0.5, 1.0, and 1.5 mM in a pH range of ~ 2 to ~ 12 . Each 1 mL of HFO suspension (1 mg mL^{-1}) was mixed with 1.25, 2.5, or 5.0 mL of 2.0 mM silicic acid and then transferred into a plastic tube. Using different ratios of 0.5 M NaCl, HCl, and NaOH and dilution with DI H₂O as described above, we obtained different targeted pH values from ~ 2 to ~ 12 at the same ionic strength (IS) of 0.05 M. In experiments measuring ζ as a function of IS, suspensions were prepared similarly, but additions of NaCl were varied to produce the appropriate range of IS and pH 6. In the obtained suspensions, the final HFO concentration was 0.1 mg mL^{-1} , whereas silicic acid concentrations were 0.25, 0.5, and 1.0 mM. A subsample of 1.0 mL was then directly transferred into a DTS1070-folded capillary cell and ζ was measured in triplicate with the Malvern Zetasizer.

2.2.2. Dynamic light scattering

Suspensions of silicic acid and HFO at different pHs and ionic strengths were

prepared in the same manner as those used for ζ determination (see 2.2.1). Hydrodynamic diameters of particulates in suspensions of silicic acid and HFO at different pH and IS values were examined according to Kretzschmar et al. (1998) using a Malvern Zetasizer Nano ZS (UK). The detector was positioned at an angle of 173° to collect back scatter signals. In order to observe the evolution of HFO aggregates (changes in hydrodynamic diameter of particles in suspension, d_h) over time, the mean size was calculated by averaging d_h values (nm) obtained each minute. These averages were plotted over a period of 20 min.

2.2.3. Colloidal stability in test tube experiments

Colloidal stability of the HFO in the presence of the silicic acid as a function of pH was evaluated in plastic test tubes following the procedure of Lagaly et al. (1997). Using procedures similar to those described in 2.2.1, 0.2 mg mL^{-1} HFO suspensions were prepared over a target pH range and silicic acid concentrations of 0.0 to 1.4 mM. The suspensions were vortexed for 60 s to maximize particle dispersion and then held statically for 24 hours. An amount of 3 mL of each suspension was sampled from the surface of the suspension. The transmittance (%T) was determined using a UV-VIS spectrophotometer (Shimadzu, UV-2101PC) at a wavelength of 380 nm and then converted into HFO amount in suspension (in %).

3. Results

3.1. Surface charge of silicic acid suspensions

Our silicic acid solution included monomeric and/or polymeric forms in true solution, in addition to nanoparticulate polymers able to pass through a $0.45 \mu\text{m}$ filter. Our ζ measurements for silicic acid are

likely primarily those of the nanoparticulate silicic acid polymers. The pH dependence of ζ at different silicic acid concentrations is depicted in Figure 2. At $\text{pH} < 6$, the near-neutral surface charge was observed at all three concentrations of silicic acid and ζ was maintained near 0 mV. For the silicic acid concentration of 0.5 mM, a substantial decrease in ζ occurred at $\text{pH} 6.0$ to 7.5 , with the minimum ζ value of -18.5 mV found at $\text{pH} 7.5$. With a change in pH from 7.5 to 9.0 , the surface charge became less negative and ζ increased from -18.5 to -2.0 mV. For silicic acid concentrations of 1.0 and 1.5 mM, decreases in ζ were observed at pH from 6 to 9 , in which minimum values of ζ were -20.0 and -22.0 mV, found at $\text{pH} 8.6$ and 9.0 , respectively. At $\text{pH} > 9$, increases in ζ were found for silicic acid at both concentrations of 1.0 and 1.5 mM.

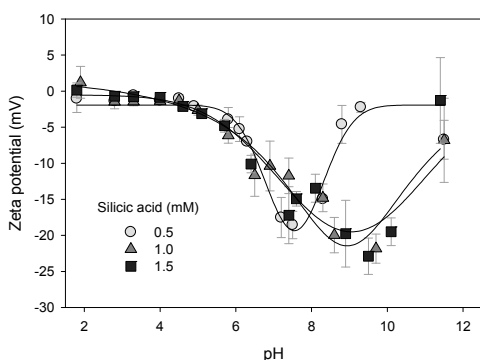


Figure 2. Zeta potential measured for silicic acid at concentrations of 0.5 , 1.0 , and 1.5 mM as a function of pH in the presence of 0.05 M NaCl as the background electrolyte. Mean values with standard deviations appear as error bars of zeta potential

3.2. Surface charge and aggregation of silicic acid - HFO suspensions

The pH dependence of ζ , determined in HFO suspensions and in the presence of

different silicic acid amounts, is shown in Figure 3a. Clearly, the presence of silicic acid resulted in decreases in the ζ of HFO over a pH range from 2 to 9 . At $\text{pH} < 6$, HFO bears a positive surface, even in the presence of up to 1.5 mM silicic acid. At $\text{pH} < 4$, relatively constant ζ of 20 , 19 , 17 , and 15 mV was observed at silicic acid concentrations of 0 , 0.5 , 1.0 , and 1.5 mM, respectively. Substantial decreases in ζ were observed at $\text{pH} 5$ - 9 . A pH change from 5 to 9 resulted in ζ decreases from 20 to -16 , 19 to -19 , 17 to -19 , and 15 to -20 mV for suspensions at silicic acid concentrations of 0 , 0.5 , 1.0 and 1.5 mM, respectively. Under each pH condition < 10 , silicic-acid-amended HFO suspensions consistently exhibited lower ζ compared to pure HFO (prepared in deionized water). The charge reversal point (i.e. iep) was at $\text{pH} 7.5$ for pure HFO, while lower iep values (7.0 , 6.4 , and 6.2) were found for silicic-acid-amended HFOs. At $\text{pH} > 10$, ζ was approx. -17 mV and no notable difference was observed among silicic acid concentrations. In this way, by shifting the HFO iep to lower pH values, silicic acid can be seen to change the aggregation properties of HFO.

The aggregation of pure HFO in the presence of silicic acid at 3 different concentrations as a function of pH is illustrated in Figure 3b. For pure HFO, d_h increased over a pH range of 2 to 8 , and decreased at $\text{pH} > 8$. At $\text{pH} 8$, a peak aggregation was observed in which d_h reached 6700 nm. Upon adsorption of silicic acid, the d_h for HFO suspensions decreased and peak aggregation shifted to lower pH s. Maximum d_h values (5200 , 4700 , and 4300 nm) were found at $\text{pH} 7.0$, 6.3 , and 6.2 in the presence of silicic acid at concentrations of 0.5 , 1.0 , and 1.5 mM, respectively.

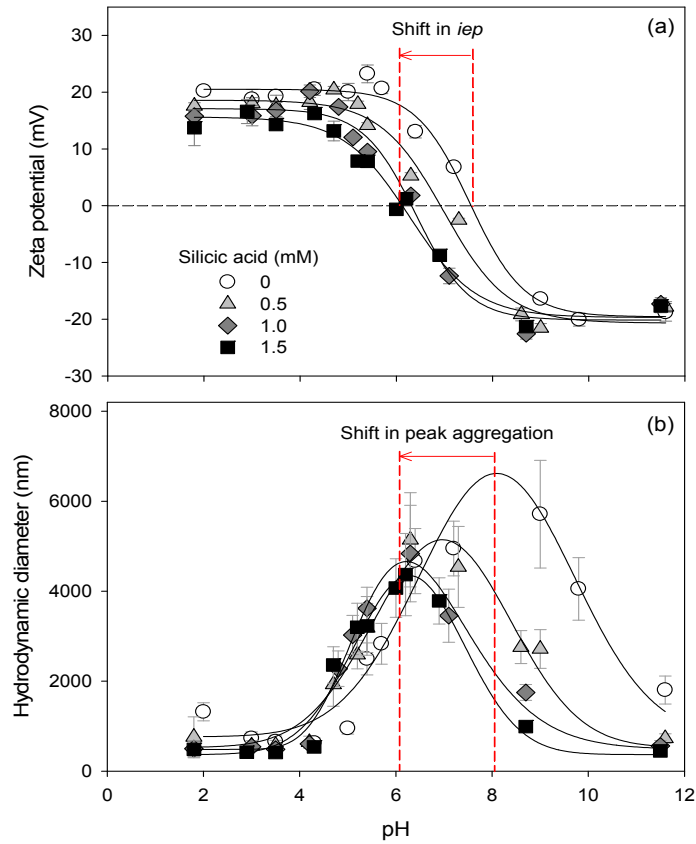


Figure 3. Zeta potential (a) and hydrodynamic radius (b) measured for HFO as a function of pH in the presence of 0.05 M NaCl as the background electrolyte. Error bars depict changes in hydrodynamic diameter of HFO aggregates measured at minute intervals over a 20 min period

Aggregation and ζ measurements of HFO at pH 6 as a function of ionic strength for four systems that vary in silicic acid concentrations are shown in Figure 4. Positive ζ values were observed across the range of ionic strength from 0.0005 to 0.5 M, but ζ became less positive upon addition of silicic acid (Figure 4a). With an increase in ionic strength from 0.0005 to 0.5 M, ζ decreased from 24.7 to 11.6, 23.5 to 5.2, 17.5 to 6.6, and 8.3 to 4.9 mV for suspensions containing silicic acid concentrations of 0, 0.5, 1.0, and 1.5 mM, respectively. These decreases in ζ are the probable explanation for the acceleration of HFO aggregation observed when ionic

strength was increased. For suspensions with silicic acid concentrations of 0, 0.5, and 1.0 mM, increasing ionic strength resulted in strong aggregation of HFO (Figure 4b). With a change of ionic strength from 0.0005 to 0.1 M, d_h values increased from 560 to 3510, 770 to 2870, and 1970 to 3510 nm for suspensions containing silicic acid concentrations of 0, 0.5, and 1.0 mM, respectively. In the presence of 1.5 mM silicic acid, d_h was relatively high at low IS and no clear change in d_h was seen as IS was increased from 0.0005 to 0.5 M. At a range of ionic strength from 0.1 to 0.5 M, only minor differences in d_h were observed for different silicic acid concentrations.

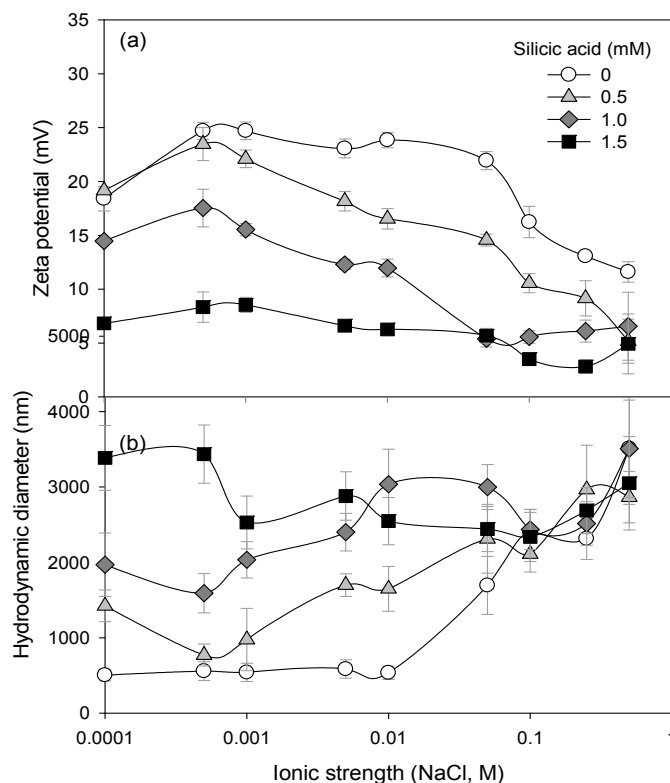


Figure 4. Zeta potential (a) and hydrodynamic radius (b) measured for HFO as a function of ionic strength in the presence of 0.05 M NaCl as the background electrolyte. Error bars illustrate the changes in hydrodynamic diameter of HFO aggregates measured every minute over a 20 min period

3.3. Colloidal stability

A 3D-graph with color gradient and mesh representing the amount of suspended colloids remaining in suspension (Figure 5) illustrates the aggregation of HFO in the presence of the silicic acid as a function of pH. At pH < 3, HFO completely dissolved within a few hours. This was due to the high solubility of fine HFO particles in acidic condition as reported by Lindsay (1979) and Kuma et al. (1992). At pH > 3, the amphoteric properties of HFO were apparent, with HFO dispersed when bearing positive or negative surface charges, and aggregated around its iep. After 24 h, three different statuses of the HFO suspensions could be observed: steric stabilization (% colloid > 90), aggregation (%

colloid < 10), and transition status (10 < % colloid < 90). Aggregation of HFO appears highly dependent on pH, and the effect of silicic acid varies within the pH range. At pH < 5.5, increases in silicic acid concentration did not have a clear effect on HFO aggregation. The stable dispersion was observed across the range of silicic acid concentration from 0 to 1.5 mM. Aggregation status for all silicic acid concentrations occurred in the pH range from 5.5 to 7.5. At pH > 7.5, HFO suspension status ranged from steric stabilization to aggregation depending on the silicic acid concentration. The silicic acid concentration of 0.8 mM or higher resulted in a stable dispersion, whereas aggregation was favored at silicic acid concentrations below 0.8 mM.

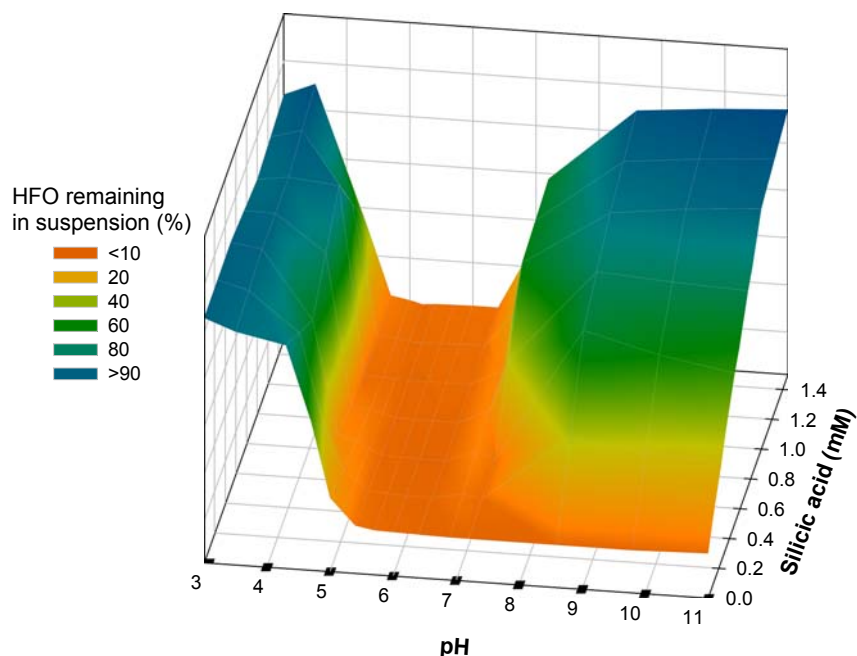


Figure 5. 3D graph created from the transmission data of the HFO suspension as functions of pH and silicic acid concentration, established after 24 h. Values shown for the % of HFO remaining in suspension include the HFO dissolved at low pH as described in the text

4. Discussion

In natural waters, silicic acid occurs almost exclusively in the form of the monomer ($\text{Si}(\text{OH})_4$) or dimer ($\text{Si}_2\text{O}_2(\text{OH})_5^-$) (Svensson et al., 1986; Dietzel, 2000). Variation in protonation/deprotonation and/or polymeric condensation can potentially yield other dissolved species (e.g. oligomeric silicic acids) (Iler, 1979; Dove and Rimstidt, 1994; Davis et al., 2002). pH and ionic strength can affect transformation of these species by changing their degree of protonation or deprotonation and resultant charge (Icopini et al., 2005). Our experiments at 0.05 M NaCl ionic strength (Figure 2) demonstrate that the surface charge of silicic acid suspensions changes significantly depending upon its concentration and pH. At $\text{pH} < 6$, ζ is close to a zero-charge point for silicic acid suspensions at a concentration range of 0.5 to 1.5 mM, indicating almost complete

protonation. This result is consistent with previous findings (Dietzel, 2000) in which silicic acid was reported to be neutral at acidic pHs. At $\text{pH} > 6$, negative charges can develop from the formation of polymeric silicic acid nanoparticles (Iler, 1979; Svensson et al., 1986; Dietzel, 2000), followed by deprotonation under alkaline condition (Icopini et al., 2005). At $\text{pH} > 6$, ζ decreases as silicic acid deprotonates, but increases again in extreme alkaline pH with a high concentration of Na^+ ion in solution, possibly due to Na^+ adsorption. When silicic acid deprotonates, its adsorption onto Fe oxides through ligand exchange (Hiemstra et al., 2007) could be a consequence. Therefore, as an adsorbing species, silicic acid could modify surface charge and affect the colloidal stability of HFO.

The iep of silicic-acid-amended HFO was observed at pH 7.5 (Figure 3a), and peak aggregation was also observed near this pH

value (Figure 3b). This overlap suggests that aggregation of HFO is manipulated by neutralization of the net charge at the iep. Since electrostatic repulsion is minimized at the iep, aggregation can be induced since attractive Van der Waals forces prevail (Cornell and Schwertmann, 1996). At pH levels below the iep of 7.5, HFO appeared as positively charged particles due to the presence of protonated Fe-OH_2^+ groups on its surface (Figure 3a). These protonated groups can serve as positive charges and support an interaction with either anions or neutral substances in the surrounding solution (Lützow et al., 2006; Hiemstra et al., 2007). Adsorption of silicic acid onto HFO lowered the ζ of HFO and shifted the iep of HFO to lower pH values, enabling HFO to aggregate at lower pH as illustrated in Figure 3b. Above the iep of 7.5, HFO became negatively charged as Fe-OH_2^+ groups were converted to Fe-O^- groups. Dispersion of HFO in response to increases in pH resulted from the enhancement of repulsive forces between particles in the aqueous system. The presence of the deprotonated silicic acid may serve to increase negative charges for suspensions (Figure 3a), which in turn facilitates dispersion of HFO (Figure 3b). Aside from pH, ionic strength can also strongly affect aggregation of HFO by changing ζ (Figure 4). Increasing ionic strength resulted in decreases in ζ (less positive) and electronic double layer thickness, favoring aggregation. In experiments on aggregation of HFO at pH 6, no effect of silicic acid was clearly observable at high ionic strength ($[\text{NaCl}] > 0.1 \text{ M}$). In contrast, silicic acid showed a clear effect as an aggregation enhancer at low ionic strength ($[\text{NaCl}] < 0.1 \text{ M}$).

The trend in which aggregation of HFO occurred near the iep (pH from 5.5 to 7.5) was also observed in the “colloidal stability” experiments, as shown in Figure 5. However, the effect of silicic acid was more evident in

alkaline solutions ($\text{pH} > 7$), for which both aggregation and dispersion states of HFO were observed. In the presence of silicic acid up to 0.4 mM, HFO was still aggregated even at very high pH. This result could be due to a strong effect of sorption of Na^+ ions resulting in a decrease in ζ as shown in Figure 3a, as well as reduction of the double layer thickness. Consequently, HFO particles can come closer together, which favors aggregation. Increasing silicic acid resulted in a stabilizing effect on the HFO dispersion in which the region of aggregation was significantly reduced at higher pHs. With an increase of silicic acid to 0.8 mM, the full dispersion was observed over the pH range from 7.5 to 11. In contrast, the dispersion state was stabilized at $\text{pH} < 5.5$, and the presence of silicic acid did not result in aggregation in the HFO suspension. Generally, the presence of silicic acid expanded the dispersion zone of HFO as depicted in Figure 6, which implies that silicic might affect a number of processes involving HFO in nature, including colloid mobilization, coagulation, and iron sequestration.

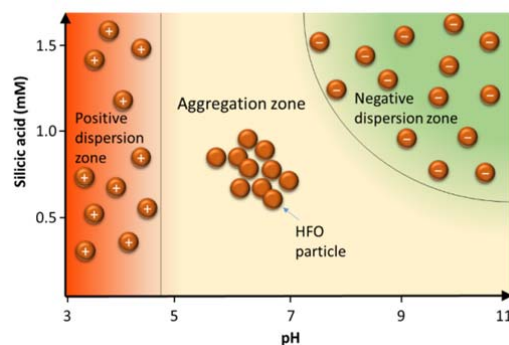


Figure 6. Schematic description of colloidal behavior of HFO in the presence of silicic acid

5. Conclusion

Silicic acid was observed to affect surface charge and aggregation of HFO over a wide

range of pH levels and ionic strength. Upon adsorption, it is likely that silicic acid lowers ζ and decreases i_{ep} , allowing HFO to aggregate at lower pH levels. The maximum aggregation of HFO under the influence of silicic acid was observed at pH 5.5-7.5, which is a typical pH value of many aqueous systems and soils. This finding suggests that silicic acid can play an important role for HFO transport in water and in the accumulation of particulate HFO in soil horizons. Understanding the effect of silicic acid on HFO aggregation is also helpful in supporting a deeper knowledge of the mobility of the pollutants loaded by Fe colloids in natural aqueous environments.

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