Influence of particle properties on iron flocculation

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ABSTRACT

In this study, the importance of charge interactions during flocculation of Fe$^{3+}$ in the presence of particles and anions/cations at various pH values was investigated. SiO$_2$ (s) and ZnO (s) were dosed as particles to promote charge interactions and/or serve as a nucleus to accelerate floc formation. In the pH range 6–9, SiO$_2$ (s) is negatively charged, while ZnO (s) carries a positive charge. Ca$^{2+}$ and HPO$_4^{2-}$ were selected to investigate charge interactions in the water phase. A significant delay in floc growth due to charge repulsion between negatively charged iron species was observed at pH$_\text{ini}$ 9. For positively charged species at pH$_\text{ini}$ 6, a delay in floc growth was observed as well, but to a lesser degree. These effects could be neutralized by either dosing (positively charged) ZnO (s) or Ca$^{2+}$ at pH$_\text{ini}$ 9, or (negatively charged) SiO$_2$ (s) at pH$_\text{ini}$ 6. The addition of phosphate did not hinder floc growth at pH$_\text{ini}$ 6. While phosphate completely inhibited floc growth at pH$_\text{ini}$ 7–9 in the presence of negatively charged SiO$_2$ (s), the presence of positively charged ZnO (s) partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing Ca$^{2+}$ partly neutralized the effect of phosphate.

Key words | charge interaction, iron flocculation, particles

INTRODUCTION

Iron chemistry is an important aspect of water treatment, where it is either added to promote removal of organic matter, heavy metals and colloidal material, or where removal of iron itself is the main goal. In the pH range 6–8, which is typical for groundwater, iron is mainly present as Fe$^{2+}$ (Jolivet et al. 2004). When groundwater is aerated, Fe$^{2+}$ oxidizes to Fe$^{3+}$, where the rate of oxidation increases for increasing pH values and stabilizes at a plateau rate at pH > 8 (Morgan & Lahav 2007). The oxidized Fe$^{3+}$ ion readily hydrolyses into Fe(OH)$^{2+}$, Fe(OH)$_2^+$, Fe(OH)$_3$(aq) or Fe(OH)$_4^-$, depending on the pH. When comparing Fe$^{3+}$ hydrolysis product speciation using hydrolysis constants from different authors, the trend seems to be that either (i) the positively charged Fe(OH)$_2^+$ dominates at pH 7, the negatively charged Fe(OH)$_3$(aq) dominates at pH 9, and pH 8 is a mixture of these, and of neutral Fe(OH)$_3$ (Liu & Miller 1999; Pham et al. 2006; Stefansson 2007), or (ii) the neutral Fe(OH)$_3$ dominates at each of these pH values (Flynn 1984; Millero & Pierrot 2007). When comparing the values for the hydrolysis constants (supporting information S1, available with the online version of this paper), it is notable that the values for Fe(OH)$_2^+$ and Fe(OH)$_4^-$ are reasonably close, which would imply that their actual concentrations are similar for all authors. Whether the concentrations of Fe(OH)$_3$(aq) are in comparison high (Flynn 1984; Millero & Pierrot 2007) or low (Liu & Miller 1999; Pham et al. 2006; Stefansson 2007) could essentially be related to the specific membrane pore size used by the authors to separate the ‘dissolved’ iron fraction from the solid fraction.

The Fe$^{3+}$ hydrolysis products will form larger complexes by binding via olation (Fe-OH-Fe) or oxolation (Fe-O-Fe) (Jolivet et al. 2004), forming nuclei and eventually growing into iron flocs. After fast hydrolysis of Fe$^{3+}$, amorphous 2-line ferrihydrite is formed (Schwertmann & Cornell 1991).

Addition of particles allows for more control of iron flocculation, as these particles may act as nucleus for flocc.
growth (Hove et al. 2009). In practical applications, the purpose of adding particles is often to increase the density of the iron flocs, which sediment more rapidly and have lower water content, and/or to accelerate floc formation (Desjardins et al. 2002; Gan et al. 2005; Gottfried et al. 2008; Hove et al. 2009; Zhou et al. 2012). In the synthesis of iron oxide nanoparticles, addition of particles (seed-mediated growth) allowed for production of more mono-disperse particles (Huang et al. 2018). While the addition of particles has proven to be beneficial, there have been limited attempts to identify the responsible mechanisms. Our aim is to investigate the importance of charge interactions during flocculation of Fe$^{3+}$ in the presence of particles.

Particles with a negative surface charge (SiO$_2$; pH$_{pzc}$ 2–3) and positive surface charge (ZnO; pH$_{pzc}$ 9.2) were selected, in order to assess the importance of charge attraction or repulsion for charged iron hydrolysis products at pH 6, 7, 8 and 9. Fe$^{3+}$ hydrolysis products should be mainly positively charged at pH 6, 7 (Fe(OH)$_2^+$), negatively charged at pH 9 (Fe(OH)$_4^-$), or a mixture of these, together with Fe(OH)$_5$ (aq) could be present at pH 8. In addition, the influence of the bivalent cations (Ca$^{2+}$) and anions (HPO$_4^{2-}$) under these experimental conditions was assessed. The influence of HPO$_4^{2-}$ and Ca$^{2+}$ on iron flocculation at pH 7 has received considerable attention (Chattelier et al. 2004; Voegelin et al. 2009, 2013; Kaegi et al. 2010; Senn et al. 2013). The research presented in this manuscript extends on this, by broadening the pH range beyond pH 7 and thereby gaining more variety in the charge of iron hydrolysis products, and by adding a particle surface with either a positive or negative surface charge.

**MATERIALS AND METHODS**

**Chemicals and stock solutions**

ZnO (>99.0%), FeCl$_3$·6H$_2$O, CaCl$_2$, NaHCO$_3$, Na$_2$HPO$_4$ were obtained from Sigma Aldrich (p.a. grade). The SiO$_2$ originated from Mol, Belgium, and was obtained from Sibelco as M32 size fraction (0.18–0.35 mm, D$_{50}$ 0.26 mm). It was ground for 60 seconds with a ring grinder (HSM100, Herzog) before use in the experiments. All stock solutions were prepared in demineralized (demi) water (Aquadem installation, Veolia, 0.09 μS/cm). The Fe$^{3+}$ solution was acidified to pH 2 to prevent flocculation. The stock solutions were dosed to obtain concentrations of 2 mg/l Fe, 150 mg/l HCO$_3^-$, 40 mg/l Ca$^{2+}$ or 1 mg/l HPO$_4^{2-}$. HCO$_3^-$ was dosed to all solutions to serve as pH buffer. The pH was adjusted with HCl or NaOH to its required value.

**Particle size distribution of SiO$_2$ and ZnO**

The particle volume distribution of ZnO and ground SiO$_2$ were measured with a Mastersizer 2000 (Malvern), coupled with a hydro 2000MU wet sample dispersion unit. This dispersion was obtained by mechanical mixing, no additional dispersants were added. The particle volume distribution of SiO$_2$ and ZnO can be found in the supporting information (S2, available with the online version of this paper). Particle counts and surface area were calculated from this data by assuming spherical particles. A fixed amount of particle surface of 0.15 m$^2$/l was dosed for either SiO$_2$ or ZnO.

**Zeta potential**

Zeta potential was measured with Zetacompact (CAD instruments), using 8.54 V/cm direct current, under the conditions (pH, conductivity) relevant in our experiments. These measurements confirmed the negative zeta potential of SiO$_2$ (supporting information S3, available online). ZnO, on the other hand, showed a positive zeta potential in MilliQ water, but a negative surface potential in the presence of HCO$_3^-$, indicating that HCO$_3^-$ adsorption might have resulted in charge reversal (Degen & Kosec 1999; Sedlak & Janusz 2008).

**Jar tests**

Jar tests were executed on a JLT6 flocculation tester (Velp Scientifica), using 1 L of solution in baffled 2 L jars. In all cases, mixing was at a constant 120 rpm, and experiments were carried out at room temperature (around 18 °C). pH values were adjusted to 6, 7, 8 or 9, and either 0.33 g/l SiO$_2$ or 0.35 g/l ZnO or no particles were dosed. ZnO powder dispersed poorly, and dispersion was aided by
using a Turrax mixer (T45N, IKA Werk) at 47.5% capacity for 5 seconds.

When SiO₂ or ZnO particles were added, a sample was taken before iron addition, and the particle size distribution was analysed with a particle counter (HIAC Royco model 9703, Pacific Scientific), where the measuring principle is based on laser obscuration. Here, 5 ml of solution was scooped from the jar and diluted in 100 ml demineralized water. This dilution may have led to floc destabilisation due to the decrease in ionic strength. The mixing rate of the particle counter sample was set to approximate the mixing rate used in the jars, and the mixing duration was kept to a minimum in an attempt to minimize floc breakage or further flocculation during analysis. Abstractions of 10 ml were done twice and were analysed by the particle counter. The results of these consecutive analyses were close, with a standard deviation less than 1% for the total amount of particles and the calculated particle volume. This indicates that further particle breakage or flocculation during analysis was limited.

Every sample measurement was followed by a rinsing step with demineralized water. Samples were taken 1, 3, 15 and 30 minutes after iron dosage. At the same time intervals, 5 ml of solution was filtered over a 0.45 μm polyethersulphone syringe filter and the total Fe concentration of the filtrate was measured. This was done photometrically (Nova Spectroquant, Merck), where iron is reduced to Fe²⁺ in thioglycolate medium and forms red-violet complexes with triazide (Fe analysis kit 1.14761.0001, Merck). The 0.45 μm filter is used to arbitrarily differentiate ‘dissolved’ from ‘solid’ iron in this study. This is no absolute definition, since solid iron particles can be formed that are smaller than 0.45 μm.

When no particles were added, the formed iron flocs could not be readily detected by the particle counter, as the measured particle counts were much lower. In these experiments, samples were filtered over a series of syringe filters (0.2/0.45/0.8 μm (nylon); 10/20 μm (polypropylene), mdi membrane technologies) and the remaining iron concentration was determined after 1, 3, 15 and 30 minutes. The pH values were only initially corrected to pH 6, 7, 8 or 9 before iron dosing, and not adjusted afterwards. These values are referred to as ‘pHini’ in this manuscript. Typical pH variation during the experiments is shown in supporting information S4 (available online).

### RESULTS AND DISCUSSION

#### No addition of particles

The size of iron oxide flocs when no particles were added was indirectly determined by filtering the sample from the jar test over a series of syringe filters in the range of 0.2–20 μm, and measuring the iron concentration in the filtrate. A decrease in iron concentrations in the filtrate indicates that iron flocs have grown to a diameter that is larger than the syringe pore size.

Floc growth after adding 2 mg/l Fe³⁺ is represented by the remaining iron concentration in the filtrate of a 0.2, 0.45, 0.8, 10 and 20 μm filter in Figure 1. For the filters <0.8 μm, iron concentrations in the filtrate were below the detection limit after 3 minutes, except at pHini 9.

Charge attraction and rapid growth is expected around the point of net zero charge. Figure 1 shows rather similar Fe³⁺ concentrations for pHini 7 and 8, which suggests that the point of net zero charge of the iron flocs could have been in between pHini 7 and 8. This is plausible, as the datasets of both Stefansson (2007) and Liu & Millero (1999) show their lowest iron oxide solubility at pH 7–7.5 at an ionic strength of 0.01 M, and Schwertmann and Cornell state that the net zero charge of iron oxides is typically within a broad pH range of 7–8 (Schwertmann & Cornell 1991).

At both extremes of the pH range, pHini 6 and 9, floc growth was delayed. At pHini 9, the initial floc growth in 0–15 minutes was delayed, while at pHini 6, the initial floc growth seems relatively comparable to pHini 7 and 8, but was delayed after 3 minutes. Pham et al. (2006) found asymmetry in ferric iron flocculation rates at pH 6 and 9 as well, and proposes different responsible mechanisms; at pH 6, the rate of H₂O-OH⁻ exchange is mainly responsible for delayed floc growth, while charge repulsion between negatively charged Fe(OH)₄ hydrolysis products delays floc growth at pH 9 (Pham et al. 2006).

#### Addition of SiO₂ and ZnO particles

When particles were added, floc growth was followed by measuring the particle size distribution. To compare the floc growth in the presence and absence of particles, the
volume increase of flocs >20 μm is presented. This can be compared with the removed Fe fraction by the 20 μm syringe filter in the experiments without particles (Figure 1, inverse trend). In addition, the amount of Fe that is removed after filtration over a 0.45 μm syringe filter was determined. These results can be found in supporting information S6–8 (available online) and typically match with the trends that are found with the particle counter.

Floc growth after adding 2 mg/l Fe³⁺ and addition of SiO₂ or ZnO at pH ini 6–9 is presented in Figure 2. The results of baseline experiments, where particle agglomeration was followed without addition of Fe are shown as a dotted line. While the same amount of Fe was used in all experiments, the volume of flocs >20 μm was considerably larger in the presence of ZnO compared to SiO₂, which may indicate that flocs with lower density were formed in the presence of ZnO.

For pH ini 6–8, the addition of SiO₂ resulted in rapidly reaching a ‘plateau’ value for the floc volume within 3 minutes (Figure 2, left), which was faster than the trends observed when no particles were dosed. The general trends observed for ZnO were more comparable with the case where no particles were present, where ‘plateau’ values were reached after about 15 minutes.

Expected charge interactions between particles and iron species are summarized in Table 1, based on the premise of electrostatic attraction between unlike charges, and – repulsion between like charges.

Due to its negative surface charge, SiO₂ should promote floc growth at pH ini 6, and delay it at pH ini 9, while For ZnO, the opposite effect is expected. Charge attraction for SiO₂ at pH ini 6, and ZnO at pH ini 9 seemed to indeed occur; for SiO₂, the highest floc volume was found at pH ini 6, while the experiments where no particles were added indicate a delay in floc growth at this pH value. At pH ini 9, floc growth was excellent for ZnO, with both rapid floc volume increase (Figure 2, right) and virtually complete Fe removal after
0.45 μm filtration at all time intervals (S 6). This would also indicate that the negatively charged Fe(OH)$_4$ is able to interact with the (positively charged) ZnO surface, and is able to replace the HCO$_3$ which is suggested to be present at the ZnO surface, as discussed in the ‘Zeta potential’ section.

Charge repulsion was less obvious. At pH$_{ini}$ 9, floc growth was clearly delayed at SiO$_2$, although the effect of charge repulsion by the SiO$_2$ surface cannot be separated from the charge repulsion between negatively charged iron species in the water phase. For ZnO, the lowest volume increase after 15–30 minutes is found at pH$_{ini}$ 6. The initial floc growth at pH$_{ini}$ 6 during 1–3 minutes does not seem to be delayed at all, but the resulting floc was fragile and was breaking up due to shear forces created by mixing at 120 rpm.

### Table 1: Overview charge interactions particle-Fe at pH 6, 7, 8, 9

<table>
<thead>
<tr>
<th>pH$_{ini}$</th>
<th>SiO$_2$</th>
<th>ZnO</th>
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<tbody>
<tr>
<td>pH$_{ini}$ 6</td>
<td>Charge Fe$^{3+}$ species</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Particle charge</td>
<td>−</td>
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<tr>
<td></td>
<td>Fe-Fe interaction</td>
<td>Repulsion Fe-Fe</td>
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<tr>
<td></td>
<td>Fe-particle interaction</td>
<td>Attraction Fe-SiO$_2$</td>
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<tr>
<td>pH$_{ini}$ 7 and 8</td>
<td>Charge Fe$^{3+}$ species</td>
<td>+/-</td>
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<td></td>
<td>Particle charge</td>
<td>−</td>
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<tr>
<td></td>
<td>Fe-Fe interaction</td>
<td>Attraction Fe-Fe</td>
</tr>
<tr>
<td></td>
<td>Fe-particle interaction</td>
<td>Both attraction/repulsion</td>
</tr>
<tr>
<td>pH$_{ini}$ 9</td>
<td>Charge Fe$^{3+}$ species</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>Particle charge</td>
<td>−</td>
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<tr>
<td></td>
<td>Fe-Fe interaction</td>
<td>Repulsion Fe-Fe</td>
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<tr>
<td></td>
<td>Fe-particle interaction</td>
<td>Repulsion Fe-SiO$_2$</td>
</tr>
</tbody>
</table>

Positive Fe or particle charge is represented by ‘+’. Negative Fe or particle charge is represented by ‘-’.

Addition of SiO$_2$, ZnO – influence of Ca$^{2+}$ and HPO$_4^{2-}$

The experimental results when Ca$^{2+}$ or HPO$_4^{2-}$ were dosed in the presence of ZnO and SiO$_2$ are shown in Figure 3.

Floc growth in the presence of Ca$^{2+}$ and SiO$_2$ was rapid at all initial pH values (Figure 3, left). The delay which was observed at pH$_{ini}$ 9 in the absence of Ca$^{2+}$ (Figure 2) was neutralized, which may confirm charge bridge formation of Ca$^{2+}$ between SiO$_2$ and Fe(OH)$_4$ and/or Fe(OH)$_4$ molecules in the water phase. Alternatively or additionally, electrostatic repulsion can be lowered due to increased charge shielding, since addition of CaCl$_2$ increases the ionic strength.

Addition of HPO$_4^{2-}$ completely stopped flocculation at pH$_{ini}$ 7–9, but did not affect flocculation at pH$_{ini}$ 6. Based on expected charge interactions (Table 2), there are two factors that can explain why flocculation was effective at pH$_{ini}$ 6 in the presence of HPO$_4^{2-}$: (i) phosphate bridges two positively charged Fe(OH)$_2$ iron species in the water phase and...
(ii) phosphate is mostly present in its monovalent form, $\text{H}_2\text{PO}_4^-\text{Ca}$, at pH 6, rather than its divalent form, $\text{HPO}_4^{2-}\text{Ca}$, at pH 7–9. Formation of (strongly) negatively charged Fe-P species is less likely at pHini 6.

For ZnO, $\text{Ca}^{2+}$ was expected to have no (charge-related) influence at pHini 6 (Table 2), and the floc volume increase was indeed roughly similar to ZnO in the absence of $\text{Ca}^{2+}$. At increasing pH values, the floc volume after 30 minutes became gradually less (Figure 3, right). While $\text{Ca}^{2+}$ did not affect the initial floc growth during 0–3 minutes, it did seem to affect the floc stability, creating flocs that were more easily broken up by shear at higher pH values, as compared to when no $\text{Ca}^{2+}$ was present. This difference was not observed for SiO$_2$, where the created flocs are stable. Since floc stability for ZnO in the presence of $\text{Ca}^{2+}$ decreases at higher pH values, and $\text{Fe(OH)}_4^-$ becomes increasingly more dominant at higher pH values, it is possible that (charge) interaction between $\text{Fe(OH)}_4^-$ and $\text{Ca}^{2+}$ reduces the interaction between $\text{Fe(OH)}_4^-$ and the positively charged ZnO surface, leading to weaker floc structures.

In contrast to SiO$_2$, HPO$_4^{2-}$ did not completely stop iron flocculation at pHini 7–9; Fe removal after 0.45 μm filtration was initially lower, but still >85% Fe was removed after 3 minutes at these pH values ($S\ 8$). This indicates that the presence of positively-charged ZnO surface can partly reverse the detrimental influence of HPO$_4^{2-}$ on iron flocculation. Similarly, addition of $\text{Ca}^{2+}$ partly neutralized this detrimental influence of HPO$_4^{2-}$, as shown in $S\ 9$, which is in accordance with existing literature ($\text{Voegelin et al.} 2009; \text{Kaegi et al.} 2010; \text{Senn et al.} 2015$).

**CONCLUSIONS**

The aim of this research was to investigate the importance of charge interactions during flocculation of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ in
the presence of particles, anions and cations at different pH values.

A significant delay in floc growth due to charge repulsion between negatively charged iron species was observed at pHini 9 when only Fe³⁺ was dosed. For positively charged species at pHini 6, a delay in floc growth was observed as well, but to a lesser degree. These effects could be neutralized by either dosing (positively charged) ZnO(s) or Ca²⁺ at pHini 9, or (negatively charged) SiO₂ (s) at pHini 6.

The addition of phosphate did not hinder floc growth at pHini 6. While phosphate completely inhibited floc growth at pHini 7–9 in the presence of negatively charged SiO₂ (s), the presence of positively charged ZnO(s) partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing Ca²⁺ partly neutralized the effect of phosphate.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Overview of charge interactions particle-Fe-Ca²⁺ at pH 6, 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>pHini 6</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Charge Fe³⁺ species</td>
<td>+</td>
</tr>
<tr>
<td>Particle charge</td>
<td>–</td>
</tr>
<tr>
<td>Fe-particle interaction</td>
<td>Attraction Fe-SiO₂</td>
</tr>
<tr>
<td>Ca²⁺ competition and charge bridging</td>
<td>Competition with Fe (+) for SiO₂ surface</td>
</tr>
<tr>
<td>HPO₄²⁻ competition and charge bridging</td>
<td>Fe-Fe bridging Fe-ZnO bridging</td>
</tr>
<tr>
<td>pHini 9</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Charge Fe³⁺ species</td>
<td>–</td>
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<tr>
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<td>HPO₄²⁻ competition and charge bridging</td>
<td>Fe-SiO₂ bridging</td>
</tr>
</tbody>
</table>

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