

## Influence of particle properties on iron flocculation

D. J. de Ridder and D. van Halem

### ABSTRACT

In this study, the importance of charge interactions during flocculation of  $\text{Fe}^{3+}$  in the presence of particles and anions/cations at various pH values was investigated.  $\text{SiO}_{2, (s)}$  and  $\text{ZnO}_{(s)}$  were dosed as particles to promote charge interactions and/or serve as a nucleus to accelerate floc formation. In the pH range 6–9,  $\text{SiO}_{2, (s)}$  is negatively charged, while  $\text{ZnO}_{(s)}$  carries a positive charge.  $\text{Ca}^{2+}$  and  $\text{HPO}_4^{2-}$  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  $\text{pH}_{\text{ini}}$  9. For positively charged species at  $\text{pH}_{\text{ini}}$  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)  $\text{ZnO}_{(s)}$  or  $\text{Ca}^{2+}$  at  $\text{pH}_{\text{ini}}$  9, or (negatively charged)  $\text{SiO}_{2, (s)}$  at  $\text{pH}_{\text{ini}}$  6. The addition of phosphate did not hinder floc growth at  $\text{pH}_{\text{ini}}$  6. While phosphate completely inhibited floc growth at  $\text{pH}_{\text{ini}}$  7–9 in the presence of negatively charged  $\text{SiO}_{2, (s)}$ , the presence of positively charged  $\text{ZnO}_{(s)}$  partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing  $\text{Ca}^{2+}$  partly neutralized the effect of phosphate.

**Key words** | charge interaction, iron flocculation, particles

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### 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  $\text{Fe}^{2+}$  (Jolivet *et al.* 2004). When groundwater is aerated,  $\text{Fe}^{2+}$  oxidizes to  $\text{Fe}^{3+}$ , where the rate of oxidation increases for increasing pH values and stabilizes at a plateau rate at  $\text{pH} > 8$  (Morgan & Lahav 2007). The oxidized  $\text{Fe}^{3+}$  ion readily hydrolyses into  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_{3,(\text{aq})}$  or  $\text{Fe}(\text{OH})_4^-$ , depending on the pH. When comparing  $\text{Fe}^{3+}$  hydrolysis product speciation using hydrolysis constants from different authors, the trend seems to be that either (i) the positively charged  $\text{Fe}(\text{OH})_2^+$  dominates at pH 7, the negatively charged  $\text{Fe}(\text{OH})_4^-$  dominates at pH 9, and pH 8 is a mixture of these, and of neutral  $\text{Fe}(\text{OH})_3$  (Liu & Millero 1999; Pham *et al.* 2006; Stefansson 2007), or (ii) the neutral  $\text{Fe}(\text{OH})_3$  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  $\text{Fe}(\text{OH})_2^+$  and  $\text{Fe}(\text{OH})_4^-$  are reasonably close, which would imply that their actual concentrations are similar for all authors. Whether the concentrations of  $\text{Fe}(\text{OH})_{3,(\text{aq})}$  are in comparison high (Flynn 1984; Millero & Pierrot 2007) or low (Liu & Millero 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  $\text{Fe}^{3+}$  hydrolysis products will form larger complexes by binding via olation ( $\text{Fe-OH-Fe}$ ) or oxolation ( $\text{Fe-O-Fe}$ ) (Jolivet *et al.* 2004), forming nuclei and eventually growing into iron flocs. After fast hydrolysis of  $\text{Fe}^{3+}$ , 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 floc

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.* 2009). 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  $\text{Fe}^{3+}$  in the presence of particles.

Particles with a negative surface charge ( $\text{SiO}_2$ ;  $\text{pH}_{\text{pzc}}$  2–3) and positive surface charge ( $\text{ZnO}$ ;  $\text{pH}_{\text{pzc}}$  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.  $\text{Fe}^{3+}$  hydrolysis products should be mainly positively charged at pH 6, 7 ( $\text{Fe}(\text{OH})_2^+$ ), negatively charged at pH 9 ( $\text{Fe}(\text{OH})_4^-$ ), or a mixture of these, together with  $\text{Fe}(\text{OH})_3$ ,  $(\text{aq})$  could be present at pH 8. In addition, the influence of the bivalent cations ( $\text{Ca}^{2+}$ ) and anions ( $\text{HPO}_4^{2-}$ ) under these experimental conditions was assessed. The influence of  $\text{HPO}_4^{2-}$  and  $\text{Ca}^{2+}$  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.* 2015). 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

$\text{ZnO}$  (>99.0%),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{HPO}_4$  were obtained from Sigma Aldrich (p.a. grade). The  $\text{SiO}_2$  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,  $0.09 \mu\text{S}/\text{cm}$ ). The  $\text{Fe}^{3+}$  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  $\text{HCO}_3^-$ , 40 mg/l  $\text{Ca}^{2+}$  or 1 mg/l  $\text{HPO}_4^{2-}$ .  $\text{HCO}_3^-$  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 $\text{SiO}_2$ and ZnO

The particle volume distribution of  $\text{ZnO}$  and ground  $\text{SiO}_2$  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  $\text{SiO}_2$  and  $\text{ZnO}$  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  $0.15 \text{ m}^2/\text{l}$  was dosed for either  $\text{SiO}_2$  or  $\text{ZnO}$ .

### Zeta potential

Zeta potential was measured with Zetacompact (CAD instruments), using  $8.54 \text{ V}/\text{cm}$  direct current, under the conditions (pH, conductivity) relevant in our experiments. These measurements confirmed the negative zeta potential of  $\text{SiO}_2$  (supporting information S3, available online).  $\text{ZnO}$ , on the other hand, showed a positive zeta potential in MilliQ water, but a negative surface potential in the presence of  $\text{HCO}_3^-$ , indicating that  $\text{HCO}_3^-$  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  $18^\circ\text{C}$ ). pH values were adjusted to 6, 7, 8 or 9, and either 0.33 g/l  $\text{SiO}_2$  or 0.35 g/l  $\text{ZnO}$  or no particles were dosed.  $\text{ZnO}$  powder dispersed poorly, and dispersion was aided by

using a Turrax mixer (T45N, IKA Werk) at 47.5% capacity for 5 seconds.

When SiO<sub>2</sub> 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 Fe<sup>2+</sup> 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 'pH<sub>ini</sub>' 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.

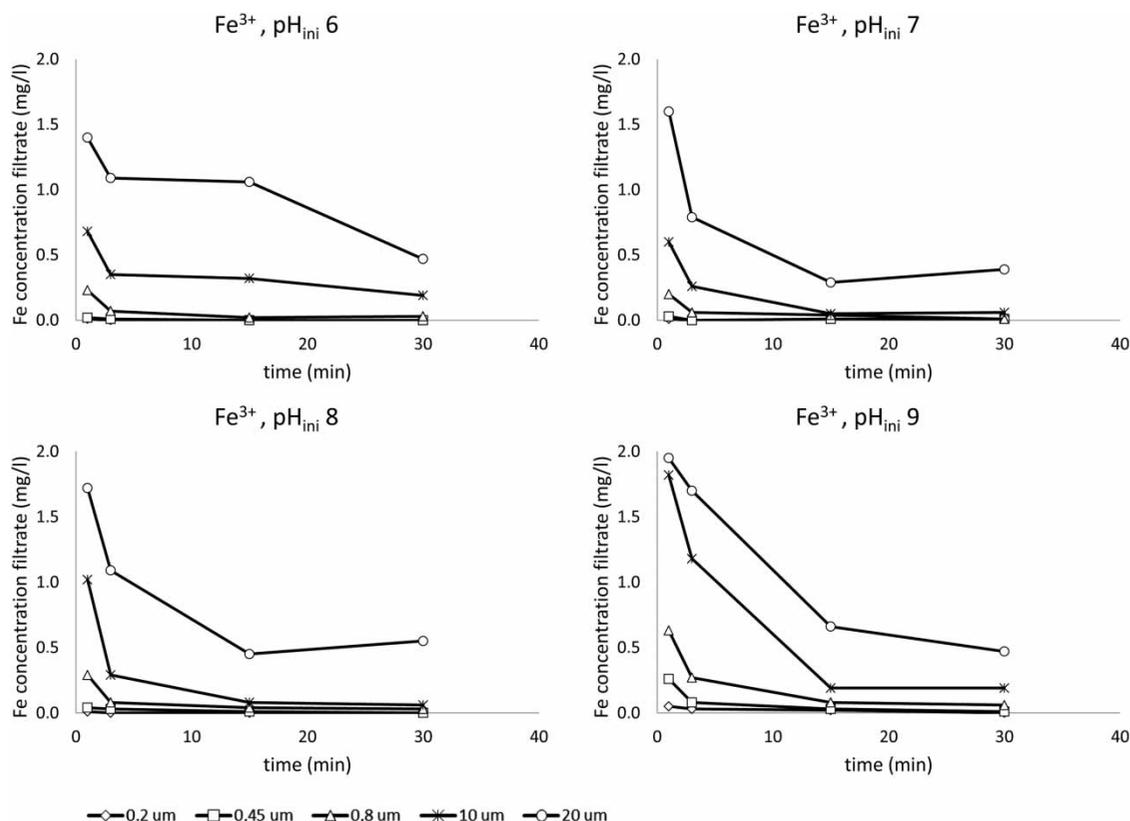
Floc growth after adding 2 mg/l Fe<sup>3+</sup> is represented by the remaining iron concentration in the filtrate of a 0.2, 0.45, 0.8, 10 and 20 µm filter in [Figure 1](#). For the filters <0.8 µm, iron concentrations in the filtrate were below the detection limit after 3 minutes, except at pH<sub>ini</sub> 9.

Charge attraction and rapid growth is expected around the point of net zero charge. [Figure 1](#) shows rather similar Fe<sup>3+</sup> concentrations for pH<sub>ini</sub> 7 and 8, which suggests that the point of net zero charge of the iron flocs could have been in between pH<sub>ini</sub> 7 and 8. This is plausible, as the data-sets 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, pH<sub>ini</sub> 6 and 9, floc growth was delayed. At pH<sub>ini</sub> 9, the initial floc growth in 0–15 minutes was delayed, while at pH<sub>ini</sub> 6, the initial floc growth seems relatively comparable to pH<sub>ini</sub> 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 H<sub>2</sub>O-OH<sup>-</sup> exchange is mainly responsible for delayed floc growth, while charge repulsion between negatively charged Fe(OH)<sub>4</sub><sup>-</sup> hydrolysis products delays floc growth at pH 9 ([Pham \*et al.\* 2006](#)).

### Addition of SiO<sub>2</sub> 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



**Figure 1** |  $\text{Fe}^{3+}$  removal after filtration with 0.2–20  $\mu\text{m}$  syringe filters at initial  $\text{pH}_{\text{ini}}$  6, 7, 8 and 9 in buffered demi water (150  $\text{mg/l}$   $\text{HCO}_3^-$ ) at 120 rpm. Initial concentration 2  $\text{mg/l}$   $\text{Fe}^{3+}$ .

volume increase of flocs  $>20 \mu\text{m}$  is presented. This can be compared with the removed Fe fraction by the 20  $\mu\text{m}$  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  $\mu\text{m}$  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.

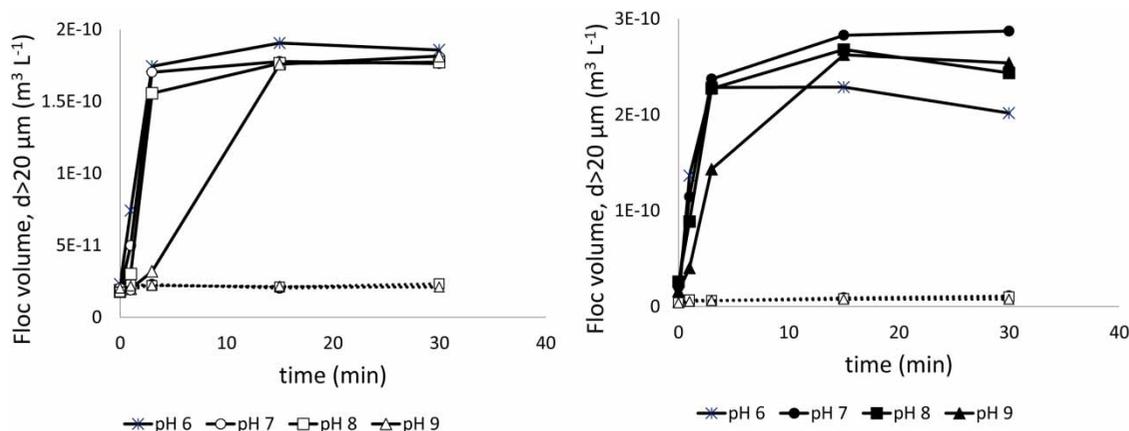
Floc growth after adding 2  $\text{mg/l}$   $\text{Fe}^{3+}$  and addition of  $\text{SiO}_2$  or  $\text{ZnO}$  at  $\text{pH}_{\text{ini}}$  6–9 is presented in Figure 2. The results of baseline experiments, where particle agglomeration was followed without addition of Fe are shown as a dotted line. While the same amount of Fe was used in all experiments, the volume of flocs  $>20 \mu\text{m}$  was considerably larger in the presence of  $\text{ZnO}$  compared to  $\text{SiO}_2$ , which may indicate that flocs with lower density were formed in the presence of  $\text{ZnO}$ .

For  $\text{pH}_{\text{ini}}$  6–8, the addition of  $\text{SiO}_2$  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  $\text{ZnO}$  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,  $\text{SiO}_2$  should promote floc growth at  $\text{pH}_{\text{ini}}$  6, and delay it at  $\text{pH}_{\text{ini}}$  9, while for  $\text{ZnO}$ , the opposite effect is expected. Charge attraction for  $\text{SiO}_2$  at  $\text{pH}_{\text{ini}}$  6, and  $\text{ZnO}$  at  $\text{pH}_{\text{ini}}$  9 seemed to indeed occur; for  $\text{SiO}_2$ , the highest floc volume was found at  $\text{pH}_{\text{ini}}$  6, while the experiments where no particles were added indicate a delay in floc growth at this pH value. At  $\text{pH}_{\text{ini}}$  9, floc growth was excellent for  $\text{ZnO}$ , with both rapid floc volume increase (Figure 2, right) and virtually complete Fe removal after



**Figure 2** | Influence of pH on floc growth ( $d > 20 \mu\text{m}$ ) with  $0.15 \text{ m}^2/\text{l}$  of  $\text{SiO}_2$  (left), and  $\text{ZnO}$  (right). Buffered demi water ( $150 \text{ mg/l HCO}_3^-$ ), 120 RPM,  $2 \text{ mg/l Fe}^{3+}$ . Dotted lines: baseline experiments ( $\text{SiO}_2$  or  $\text{ZnO}$  without  $\text{Fe}$  dose).

**Table 1** | Overview charge interactions particle-Fe at pH 6, 7, 8, 9

	$\text{SiO}_2$	$\text{ZnO}$
<b>pH<sub>ini</sub> 6</b>		
Charge $\text{Fe}^{3+}$ species	+	+
Particle charge	-	+
Fe-Fe interaction	Repulsion Fe-Fe	Repulsion Fe-Fe
Fe-particle interaction	Attraction Fe- $\text{SiO}_2$	Repulsion Fe- $\text{ZnO}$
<b>pH<sub>ini</sub> 7 and 8</b>		
Charge $\text{Fe}^{3+}$ species	+/-	+/-
Particle charge	-	+
Fe-Fe interaction	Attraction Fe-Fe	Attraction Fe-Fe
Fe-particle interaction	Both attraction/repulsion	Both attraction/repulsion
<b>pH<sub>ini</sub> 9</b>		
Charge $\text{Fe}^{3+}$ species	-	-
Particle charge	-	+
Fe-Fe interaction	Repulsion Fe-Fe	Repulsion Fe-Fe
Fe-particle interaction	Repulsion Fe- $\text{SiO}_2$	Attraction Fe- $\text{ZnO}$

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

$0.45 \mu\text{m}$  filtration at all time intervals (S 6). This would also indicate that the negatively charged  $\text{Fe}(\text{OH})_4^-$  is able to interact with the (positively charged)  $\text{ZnO}$  surface, and is able to replace the  $\text{HCO}_3^-$  which is suggested to be present at the  $\text{ZnO}$  surface, as discussed in the 'Zeta potential' section.

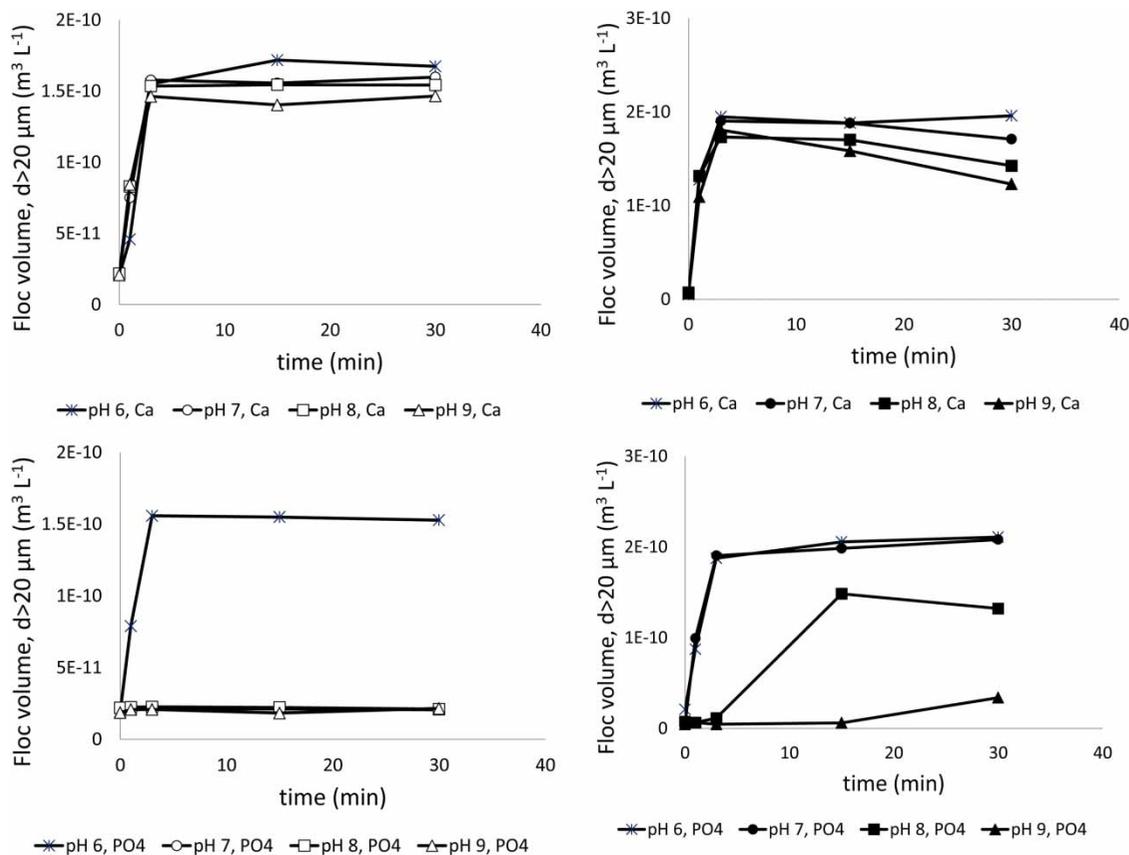
Charge repulsion was less obvious. At  $\text{pH}_{\text{ini}} 9$ , floc growth was clearly delayed at  $\text{SiO}_2$ , although the effect of charge repulsion by the  $\text{SiO}_2$  surface cannot be separated from the charge repulsion between negatively charged iron species in the water phase. For  $\text{ZnO}$ , the lowest volume increase after 15–30 minutes is found at  $\text{pH}_{\text{ini}} 6$ . The initial floc growth at  $\text{pH}_{\text{ini}} 6$  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.

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

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

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

Addition of  $\text{HPO}_4^{2-}$  completely stopped flocculation at  $\text{pH}_{\text{ini}} 7-9$ , but did not affect flocculation at  $\text{pH}_{\text{ini}} 6$ . Based on expected charge interactions (Table 2), there are two factors that can explain why flocculation was effective at  $\text{pH}_{\text{ini}} 6$  in the presence of  $\text{HPO}_4^{2-}$ : (i) phosphate bridges two positively charged  $\text{Fe}(\text{OH})_2^+$  iron species in the water phase and



**Figure 3** | Influence of pH and  $\text{HPO}_4^{2-}$  (lower graphs) or  $\text{Ca}^{2+}$  (upper graphs) dosage on floc growth ( $d > 20 \mu\text{m}$ ) in the presence of  $\text{SiO}_2$  (left hand graphs) or  $\text{ZnO}$  (right hand graphs). Buffered demi water (150 mg/l  $\text{HCO}_3^-$ ), 40 mg/l  $\text{Ca}^{2+}$ , 120 RPM, 2 mg/l  $\text{Fe}^{3+}$ .

(ii) phosphate is mostly present in its monovalent form,  $\text{H}_2\text{PO}_4^-$ , at pH 6, rather than its divalent form,  $\text{HPO}_4^{2-}$ , at pH 7–9. Formation of (strongly) negatively charged Fe-P species is less likely at  $\text{pH}_{\text{ini}}$  6.

For  $\text{ZnO}$ ,  $\text{Ca}^{2+}$  was expected to have no (charge-related) influence at  $\text{pH}_{\text{ini}}$  6 (Table 2), and the floc volume increase was indeed roughly similar to  $\text{ZnO}$  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  $\text{SiO}_2$ , where the created flocs are stable. Since floc stability for  $\text{ZnO}$  in the presence of  $\text{Ca}^{2+}$  decreases at higher pH values, and  $\text{Fe}(\text{OH})_4^-$  becomes increasingly more dominant at higher pH values, it is possible that (charge) interaction between  $\text{Fe}(\text{OH})_4^-$  and  $\text{Ca}^{2+}$  reduces

the interaction between  $\text{Fe}(\text{OH})_4^-$  and the positively charged  $\text{ZnO}$  surface, leading to weaker floc structures.

In contrast to  $\text{SiO}_2$ ,  $\text{HPO}_4^{2-}$  did not completely stop iron flocculation at  $\text{pH}_{\text{ini}}$  7–9; Fe removal after 0.45  $\mu\text{m}$  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  $\text{ZnO}$  surface can partly reverse the detrimental influence of  $\text{HPO}_4^{2-}$  on iron flocculation. Similarly, addition of  $\text{Ca}^{2+}$  partly neutralized this detrimental influence of  $\text{HPO}_4^{2-}$ , as shown in S 9, which is in accordance with existing literature (Voegelin *et al.* 2009; Kaegi *et al.* 2010; 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

**Table 2** | Overview of charge interactions particle-Fe-Ca<sup>2+</sup> at pH 6, 9

	SiO <sub>2</sub>	ZnO
pH <sub>ini</sub> 6		
Charge Fe <sup>3+</sup> species	+	+
Particle charge	-	+
Fe-particle interaction	Attraction Fe-SiO <sub>2</sub>	Repulsion Fe-ZnO
Ca <sup>2+</sup> competition and charge bridging	Competition with Fe (+) for SiO <sub>2</sub> surface	
HPO <sub>4</sub> <sup>2-</sup> competition and charge bridging	Fe-Fe bridging	Fe-Fe bridging Fe-ZnO bridging
pH <sub>ini</sub> 9		
Charge Fe <sup>3+</sup> species	-	-
Particle charge	-	+
Fe-particle interaction	Repulsion Fe-SiO <sub>2</sub>	Attraction Fe-ZnO
Ca <sup>2+</sup> competition and charge bridging	Fe-Fe bridging Fe-SiO <sub>2</sub> bridging	Fe-Fe bridging
HPO <sub>4</sub> <sup>2-</sup> competition and charge bridging		Competition with Fe (-) for ZnO surface

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

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 pH<sub>ini</sub> 9 when only Fe<sup>3+</sup> was dosed. For positively charged species at pH<sub>ini</sub> 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<sub>(s)</sub> or Ca<sup>2+</sup> at pH<sub>ini</sub> 9, or (negatively charged) SiO<sub>2, (s)</sub> at pH<sub>ini</sub> 6.

The addition of phosphate did not hinder floc growth at pH<sub>ini</sub> 6. While phosphate completely inhibited floc growth at pH<sub>ini</sub> 7–9 in the presence of negatively charged SiO<sub>2, (s)</sub>, the presence of positively charged ZnO<sub>(s)</sub> partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing Ca<sup>2+</sup> partly neutralized the effect of phosphate.

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