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Densification of iron(III) sludge in neutralization

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Abstract

Acid mine drainage (AMD), of which iron is a substantial component, is a potential by-product in the mining industry. Conventional neutralization is a common approach to treat AMD, although it creates a major disposal problem due to the generation of voluminous sludge. Sludge recirculation improves solid density by slowing down the rate of neutralization and allowing the growth of precipitates, while existing solids act as seed particles by providing necessary surface area for precipitation. The mechanisms of iron sludge densification are not fully understood, mainly because of the complex nature of iron chemistry, and the variety of amorphous, polymeric oxides that could be formed. In this work, the effects of alkaline reagents, flocculant addition, and dosing sequence, on the precipitation of iron (III) hydroxide and densification of the recycled sludge were investigated. Slowly dissolving lime ($Ca(OH)_2$) was found to be more effective than caustic (NaOH) in producing sludge with higher solid contents. Polymers addition created stronger aggregates that could withstand shearing without significant size reduction, but the overall sludge density was lower than those produced without flocculant. Conditioning the sludge at pH between 3.5 and 4.5 by adding fresh lime in a specific dosing manner appeared to be conducive to the growth of large agglomerates. The final sludge solid content of ~15 wt.% was considerably higher than others produced under different conditions. The plate-like structures of precipitates generated with more recycles in this instance, possibly helped ease the release of entrapped water between solids during shearing, thus producing sludge with higher solid density.

Keywords: neutralization; iron hydroxide; precipitation; pH; sludge recycle; densification

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1. Introduction

Iron is one of the most abundant metals found in a variety of ores with other elements. Iron pyrite (FeS_2) is a sulfide-containing compound often uncovered during a mining process. The pyrite oxidizes upon contact with air and water, and reacts

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to form ferric hydroxide precipitant and sulfuric acid (Silver, 1993)

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow 2H_2SO_4 + Fe(OH)_3 \tag{1}$$

The products, also known as acid mine drainage (AMD), are detrimental to the environment. Conventional neutralization of AMD involves increasing the pH of the waste streams to a specific value, depending on which metals are to be removed. For AMD with a ferrous iron component, air is frequently injected for oxidation, producing a more chemically stable ferric iron sludge. The process often creates a voluminous sludge with solids concentration as low as 1%, particularly when treating effluents with low solid loadings (Fig. 1(a)).

Chemicals that are ordinarily used to neutralize AMD include lime ($Ca(OH)_2$), limestone ($CaCO_3$), hydroxides ($Mg(OH)_2$, NaOH), sulfides (Na_2S, NaHS, CaS), and ammonia (NH_3). Lime is the traditional choice in industry due to its high pH value, requiring only a reasonable reaction time for simultaneous formation of metal hydroxides and calcium sulfate (gypsum)

$$Ca(OH)_2 + M^{2+}/M^{3+}H_2O + H_2SO_4 \rightarrow M(OH)_2/M(OH)_3 + CaSO_4 + H_2O \tag{2}$$

To increase the sludge solid content, a sludge recycle process (Fig. 1(b)), known as the High Density Sludge (HDS) process, was invented (Kostenbader and Haines, 1970). The process is thought to remove free water molecules by altering particle structures or by forming precipitates with fewer water molecules per solid particle; giving a more compact, hydrophobic sludge. The geochemical stability of the precipitates is also favored when there is a high iron to total metals ratio in the plant feed. The sludge solid content (around 10–30%) is generally much higher than a conventional neutralization process (Kuyucak, 1998). The initial work indicated that the process

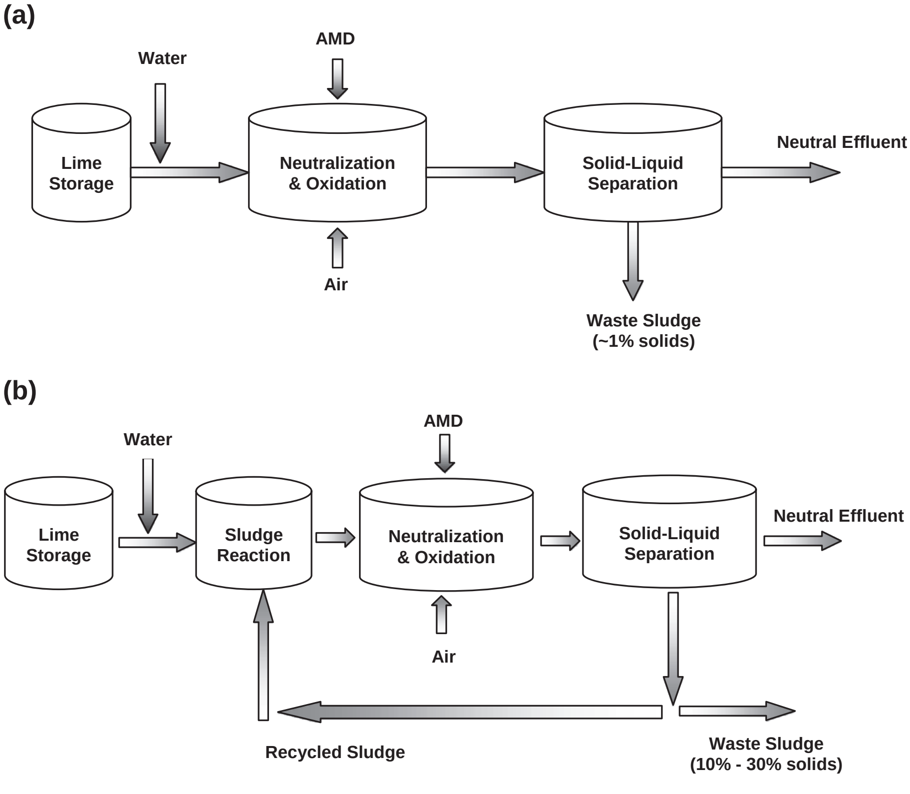

Fig. 1. Schematics of (a) conventional neutralization and (b) neutralization with recycle (or High Density Sludge process).

performance was considerably influenced by the ferrous to ferric iron ratio, the ratio of recycled to precipitated solids, pH, and the detention time in the reaction tank (Kostenbader and Haines, 1970). The key to process improvement was the “conditioning” of recycle sludge with alkali in the conditioning tank. Poor results were observed if the alkaline slurry, recycled sludge, and AMD were mixed in the same tank; or when AMD and recycled sludge were mixed first before introducing the alkaline reagent in a subsequent reactor.

There are several hypotheses regarding the possible causes for sludge densification during conditioning and recirculation (Fig. 1(b)). The pH of the conditioned sludge is lower that that of pure alkali. When used as a neutralizing agent, the dispersion of hydroxyl ions decelerates the pH increase during reaction, resulting in a slower precipitation rate, while the solids present from a recycled sludge act as seed particles for the precipitates to grow (Bosman, 1974). In controlled batch tests with recycle for gypsum precipitation, Tapsell et al. (2001) found that stirring produced denser sludge, regardless whether the recycled sludge was conditioned with lime prior to or during neutralization. The observation implied that shearing assisted in releasing free water molecules trapped between solid layers of the gypsum crystal structure. Aging could also thicken the sludge through structural changes towards a more crystalline phase; or more likely, by expulsion of weakly bonded water in conjunction with chemical conditioning and physical means, such as dewatering or drying (Georgaki et al., 2004).

In this project, iron(III) sludge densification was studied by the precipitation and recycling of iron hydroxide from aqueous $FeCl_3$ solution. The effects of different alkaline reagents, conditioning procedures, and operating pH, on the final solid contents were observed, in order to identify factors crucial for improving sludge density.

2. A brief overview of iron(III) chemistry

A brief look at iron(III) chemistry is given here. A more comprehensive overview can be found elsewhere (Silver, 1993, Jambor and Dutrizac, 1998, Jolivet et al., 2004).

In aqueous solution, ferric ions exist as octahedral complexes $[Fe(OH_2)_6]^{3+}$ that hydrolyze by sequentially replacing the water molecules with hydroxyl ions as pH increases (Duan and Gregory, 2003)

$$Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2^{+} \rightarrow Fe(OH)_3 \rightarrow Fe(OH)_4^{-}. \tag{3}$$

The degree of polymerization depends on the hydroxides to iron ratio, the presence of anions, as well as heat and temperature, with iron oxides and oxy-hydroxides as the main hydrolysis products. Dimeric ($Fe_2(OH)_2^{4+}$), trimeric ($Fe_3(OH)_4^{5+}$), and polynuclear hydrolysis products could also form, although these are often negligible in dilute solutions and should not significantly affect the overall metal speciation. As the acidity is lowered, the formation of an aquo hydroxo zero-charge complex serves as the precursor to the solid phase.

The birth of particles or clusters stems from the condensation of hydroxylated iron complexes in aqueous solution, which proceeds via two mechanisms to form polycationic species. In case of ferric species, this phenomenon starts rapidly from highly acidic media ($pH \geq 1$). For complexes with water molecules in the coordination sphere surrounding the cations, condensation occurs by dehydration reaction between surface inorganic hydroxyl groups (olation) and the formation of hydroxo (–OH–) bridges between neighbouring particles. If there is no water molecules in the coordination sphere (oxohydroxo complexes), the condensation takes place through a two-step associative mechanism that leads to the formation of oxo (–O–) bridges (Jolivet et al., 2004).

By adding base to the solution of iron(III) at room temperature (20 °C) and increasing pH above 3, the generation of highly hydrated, amorphous, 2-line ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) (indicated with two broad bands in X-ray diffraction pattern) is kinetically favoured. The precipitation mechanisms of ferrihydrite start with nucleation producing primary crystallites at the limit of crystal growth (spherical particles up to 10 nm in size), which then agglomerate to form larger secondary particles (50–300 nm). Aggregation between primary crystallites may occur simultaneously through bonding of the surface water molecules, which is enhanced by mixing to form aggregates in hundreds of microns range (Cornell and Schwertmann, 1996).

The ferrihydrite phase is thermodynamically unstable with poor structural organization, existing in the shape of a gelatinous dark red material with large surface area. The transformation to more stable or crystalline products depends on pH and/or temperature, which determines the preferred pathway (Jolivet et al., 2004). It occurs via in situ dehydration and local rearrangement at $5 \leq pH \leq 8$ where the solid solubility is very low (around 10^{-10} mol/L). Ferrihydrite slowly changes to a more ordered structure (4- to 6-line XRD) and subsequently, to small particles of hematite (α-Fe_2O_3) with heat and time (Schwertmann et al., 1999). When the solid solubility is higher at pH<4 or pH>8, the transformation ensues slowly through dissolution and crystallization at room temperature, forming goethite (α-FeOOH) with needle-like or lathe structures. The time scale is shorter with increasing pH, with the reaction having a half-life of around 110–160 days at pH 6 to 7 (Schwertmann and Murad, 1983). In the presence of chloride ions ($>10^{-3}$ M), the creation of goethite is blocked, possibly as chloride ions penetrate the initial polycation species and rearrange the internal configuration of atoms. Accordingly, akaganeite (β-FeOOH) is formed with similar needle-shaped structures (Bailey et al., 1993).

3. Experiments

3.1. Materials

A solution of $FeCl_3$ at 17 g/L and pH 1.7 was used in the precipitation studies. Two alkaline reagents, caustic (NaOH, 97%) and lime ($Ca(OH)_2$) were used to neutralize this acidic liquor. Limbux lime (UK, CDS no. 10138) was stored in airtight containers at all times to prevent CO_2 absorption. The alkali slurries were prepared by mixing the required dosage in Milli-Q water with a mechanical stirrer to ensure homogeneous suspensions. In cases where a flocculant was required, 0.5 g of Magnafloc 155 powder was mixed with 3 ml acetone and 97 ml of Milli-Q water and left overnight before usage. Appropriate doses of this stock solution were diluted with Milli-Q water before being added to the process.

3.2. Methods

To produce the initial iron hydroxide sludge for recycle, four liters of $FeCl_3$ solution were neutralized. Alkaline reagent was then introduced carefully via a syringe over a 1-h period to reach a desired pH value. The neutralized slurry was stirred for a further 10 min to ensure a good turnover, and was left overnight. The supernatant was decanted before three-quarters of the sludge was used for the next stage (to maintain a recycle ratio of 3:1).

The effects of different conditioning sequences were studied for the neutralization of $FeCl_3$ with sludge recycle. In the High Density Sludge (HDS) process, fresh alkali was added gradually to the sludge and the mixture was stirred at 500 rpm for 15 min in the conditioning tank (Fig. 2(a)). The conditioned sludge was then fed as a reagent to neutralise 1 L ferric chloride solution (17 g/L) in the neutralizing tank with continuous pH monitoring. After an end point was reached, the slurry was left to mix for a further 10 min. If applicable, a flocculant was added at this stage and the mixture was stirred for another 5 min. The optimum flocculant dosages were found to be 5 mg/L and 9 mg/L for solids generated using caustic and lime, respectively, based on standard jar tests. The use of flocculant was aimed primarily to assist the settling of voluminous sludge, such as those produced at the early stage of the process. The weight of the slurry was recorded, before a quarter was carefully siphoned out and used for settling tests. The tests were conducted at every four recycles using a 1 L graduated cylinder with a mechanical rake to assist sludge compaction. The remaining slurry was allowed to settle for 1.5 h before the supernatant was decanted. The settled sludge and decant liquor were weighed, and the sludge was then recycled back to the conditioning tank. The process was repeated with a recycle ratio of 3:1, until recycle number 28 was reached.

In the Recycle to Conditioning Tank (RCT), alkali was added together with iron chloride in the neutralization tank, after shearing the recycled sludge at 500 rpm for 15 minutes in the conditioning tank (Fig. 2(b)). In the 2-stages process, fresh iron chloride and a portion of the alkali reagent were added in the first neutralization tank, while the rest of the alkali was added in the second tank to reach the end point pH.

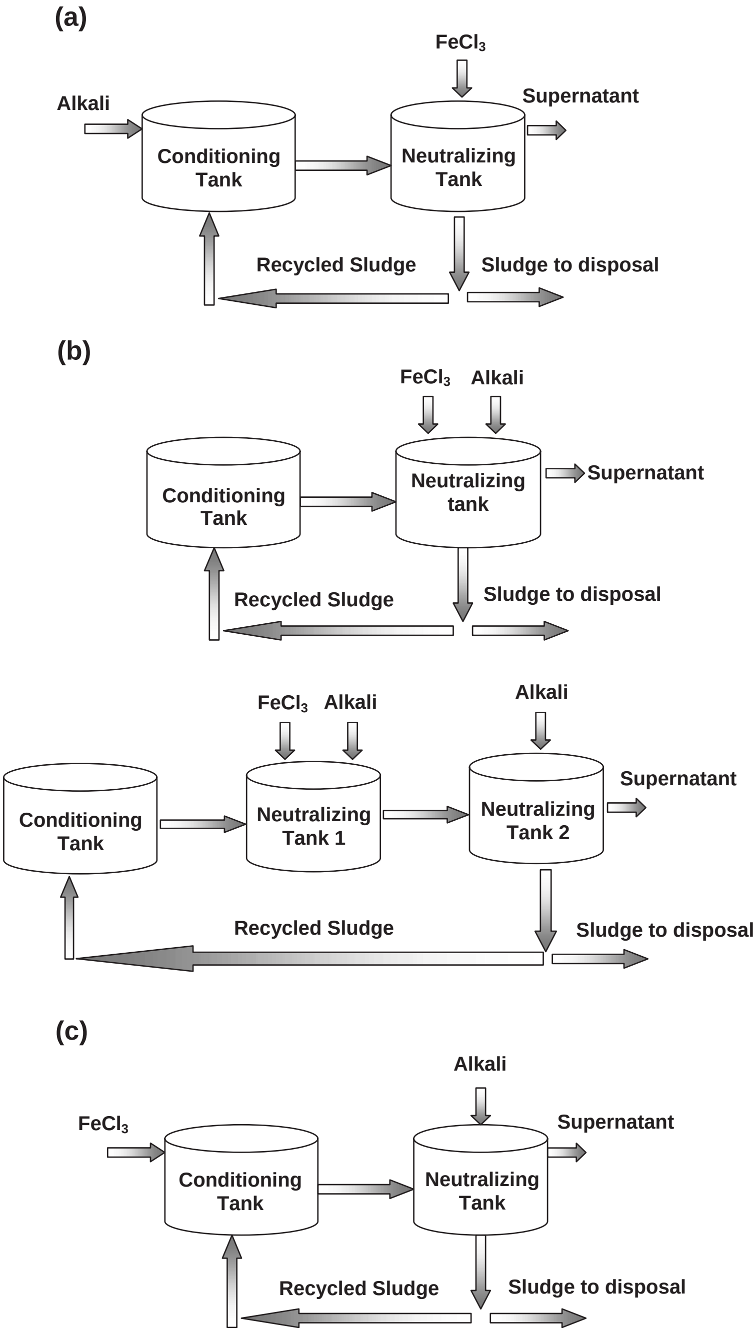

Fig. 2. Dosing sequences for (a) High Density Sludge (HDS), (b) Recycle to Conditioning Tank (RCT) in single and two stages, and (c) Conditioning with Iron Chloride (CIC).

For Conditioning with Iron Chloride (CIC), the recycled sludge was first mixed with fresh iron chloride for 15 min before alkali was added (Fig. 2(c)). Similar sampling and measurement procedures were adopted in all experiments. The size distribution of sludge particles was measured using a light scattering instrument, Malvern Mastersizer S, where solids in their supernatant were placed in a batch cell and stirred with magnetic stirrer during measurement to keep them in suspension. A Leica optical microscopy combined with CCD camera was used to capture the image of solids in suspension. Some of the dried sludge samples were analyzed with X-ray diffraction (XRD) to identify their solid phase and crystallinity, whereas morphological information on the precipitates was obtained using Transmission Electron Microscopy (TEM).

4. Results and discussions

Tests HDS-1 and HDS-2 compared iron hydroxide sludges produced using caustic (NaOH) to pH 8 according to the HDS recycle mode (Table 1). Marginal improvements from initial neutralization in sludge solid content of around 0.5 wt.% and 2.0 wt.% for 15 min and 30 min dosing periods, respectively, were observed (Fig. 3). The precipitation of iron hydroxide in a chloride media proceeds via the hydration of alkaline (lime) solid particles, followed by dissolution and dissociation of hydroxyl ions, and hydrolysis of ferric monomers. Subsequently, short chain polymeric species of iron are formed, leading to the precipitation of iron hydroxide (Jamieson et al., 2003). When using strong bases such as NaOH, the hydroxyl ions are dissolved readily in water such that the reaction between ferric ions and the fully dissociated OH– ions occurs instantaneously, resulting in a mass generation of nuclei. The rapid precipitation rate produces a vast number of small particles with a limited opportunity to grow before the reaction reached equilibrium (Bosman, 1974). It has been proposed that fast nucleation and crystallization rates (higher supersaturation) result in increasing randomness for aggregation/agglomeration to secondary particles, therefore forming more irregular and open precipitates (Loan et al., 2002). Extending the sludge dosing period from 15 to 30 min only resulted in a slight increase of the final solid content. Accordingly, the period of alkali addition for neutralization with caustic did not have a significant effect on the reaction rate.

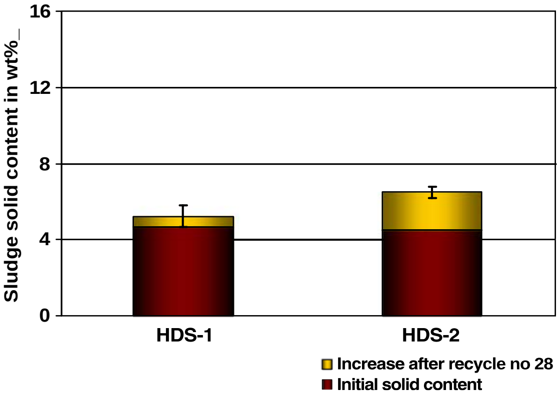

Fig. 3. Increase in sludge solid content from initial neutralization to final recycle step for HDS process with NaOH (caustic).

A third test (HDS-3) utilising lime as the alkaline reagent (Table 2) showed an increase of almost 3 wt.% after 28 recycles, albeit with a lower end point pH of 6 attained within a comparable dosing time, due to the slower reaction rate of lime (Fig. 4). When lime conditioned sludge was added to the neutralizing tank, there would be an immediate reaction between dissociated hydroxyl ions from lime and ferric ions. After the free hydroxyl ions were used up, dissolution and dissociation of lime needed to occur before further reaction. Accordingly, a comparatively slower lime reaction rate decelerated the formation of iron hydroxides and encouraged the transformation from voluminous precipitates to denser solids, aided by surface precipitation on existing sludge particles. However, the increase in iron sludge solid content was still much poorer than when a similar HDS recycle mode with lime was applied to gypsum precipitation (Tapsell et al., 2002). In their case, an

Table 1
Experimental conditions for iron(III) neutralization with caustic (NaOH) through High Density Sludge (HDS) process

Experiment	Reagent	Dosing manner	Dosing time (min)	Flocculant dosage (mg/L)	End point pH
HDS-1	30 wt.% NaOH	Even[a]	15	5	8
HDS-2	30 wt.% NaOH	Even	30	5	8

[a] Equal parts added every 5 minutes interval.

Table 2
Experimental conditions for iron(III) neutralization with lime ($Ca(OH)_2$) through High Density Sludge (HDS), Recycle to Conditioning Tank (RCT), and Conditioning with Iron Chloride (CIC) processes

Experiment	Reagent	Dosing manner	Dosing time (min)	Flocculant dosage (mg/L)	End point pH
HDS-3	20 wt.% $Ca(OH)_2$	Even	30	9	6
RCT-1	20 wt.% $Ca(OH)_2$	Even	30	9	6
CIC	20 wt.% $Ca(OH)_2$	Even	30	9	6

improvement of around 15 wt.% in solid content could be observed at 24 recycles.

Different conditioning modes were subsequently applied. RCT-1 was conducted using equal amounts of lime distributed evenly during the dosing period as the HDS series, but according to the Recycle to Conditioning Tank (RCT) sequence. Here the recycled sludge was subjected to shearing on its own in the conditioning tank, while alkali and $FeCl_3$ were added afterwards in the neutralization tank (Fig. 2(b)). In the Conditioning with Iron Chloride (CIC) test, the effect of acidic conditioning on iron hydroxide precipitation was investigated by mixing fresh $FeCl_3$ with recycled sludge in the conditioning tank for 15 min before neutralization (Fig. 2(c)). The results indicated that RCT could improve the sludge solid content comparatively better than HDS, while CIC showed an equal or lower increase relative to HDS within the margin of error. Conditioning the recycled sludge of pH 6 with strongly acidic $FeCl_3$ (at pH<2), as in the CIC mode, would cause some of the existing ferric hydroxide precipitates to de-hydrolyse back to soluble poly-cations due to the decrease in pH. As lime was added gradually to the conditioned sludge, surface reaction on existing sludge particles, as well as formation of new particles would occur. When the sludge was subjected to the subsequent recycle route, the acidic environment in the conditioning tank could easily dissolve the small particles generated in the previous step, while simultaneously eroding the larger agglomerates, although these would probably re-grow during neutralization. Hence, prolonged contact time between iron(III) sludge and acid was likely to be detrimental to precipitate growth and consequently, sludge density.

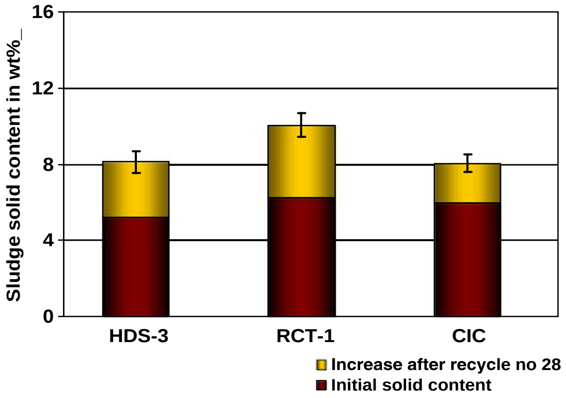

Fig. 4. Increase in sludge solid content from initial neutralization to final recycle step for HDS, RCT, and CIC processes with $Ca(OH)_2$ (lime).

In RCT sequence of conditioning, the recycled sludge at pH 6 would be slightly positive relative to the point of zero charge for iron (III) oxides and hydroxides (pH 6.6–8.2) (Duan and Gregory, 2003). Shearing in the conditioning tank had possibly increased the sludge surface area. As the sludge was mixed with ferric chloride solution in the neutralizing tank, chloride ions would be attracted to the solids' surface, followed by ferric ions. When lime was added to the neutralizing tank, the sludge particles acted as nuclei endorsing size growth, by attracting hydroxyl ions to positively charged iron species, inducing precipitation and successively replacing the chloride ions. A series of RCT tests was subsequently conducted to investigate the effects of different alkaline dosing methods and the use of flocculant with this mode of sludge recycle (Table 3). A single neutralization vessel (in conjunction with a conditioning tank) was used in RCT-1 to RCT-4, whereas two neutralization tanks were utilised for RCT-5. More than half the total amount of lime was added within 5 min of dosing time for RCT-2 (uneven addition), while the remainder was distributed equally over the remaining period. In RCT-3, the lime was added in a similar manner as in RCT-1 (even addition) but without the use of flocculant in the process. For fast

Table 3
Experimental conditions for iron(III) neutralization with lime ($Ca(OH)_2$) through Recycle to Conditioning Tank (RCT) process

Experiment	Reagent	Dosing manner	Dosing time (min)	Flocculant dosage (mg/L)	End point pH
RCT-1	20 wt.% $Ca(OH)_2$	Even	30	9	6
RCT-2	20 wt.% $Ca(OH)_2$	Uneven[a]	30	9	6
RCT-3	20 wt.% $Ca(OH)_2$	Even	30	–	6
RCT-4	20 wt.% $Ca(OH)_2$	Fast	N/A	–	6
RCT-5	20 wt.% $Ca(OH)_2$	Fast 2-stage[b]	N/A	–	2.5–3 (1st stage) 6 (2nd stage)

[a] 60% added over the first 5 minutes and the remainder distributed equally every 5 minutes interval.

[b] 60% added initially, and 40% at 20 minutes.

addition (RCT-4 and RCT-5), the lime was added instantaneously in single doses.

The highest improvement in sludge solid content occurred for RCT-2 when lime was added unevenly (Fig. 5). The average size of sludge particles in RCT-2 increased from ~37 μm to ~118 μm from initial neutralization to final recycles. On the other hand, the trends displayed by other RCT tests, as well as HDS and CIC series, indicated either a decrease or less significant increase in average particle sizes (Table 4). Optical images of solids in suspension showed that the agglomerates generated in RCT process after 28 recycles were much larger and denser than those produced from HDS or CIC tests (Figs. 6–8).

A comparison of mean particle sizes from RCT-1 and RCT-3 demonstrates that flocculant addition in RCT-1 could better preserve the particle size in successive recycles, possibly by producing stronger aggregates that were not easily fragmented by shearing, either from the process or during size measurement with Malvern Mastersizer S (where the particles have to be continuously kept from settling by stirring the suspension). Nonetheless, the final solid content was lower in the presence of flocculant (Fig. 5), because the packing of aggregate networks would be less compact than a configuration of small, dense precipitates contained within equal sludge volumes.

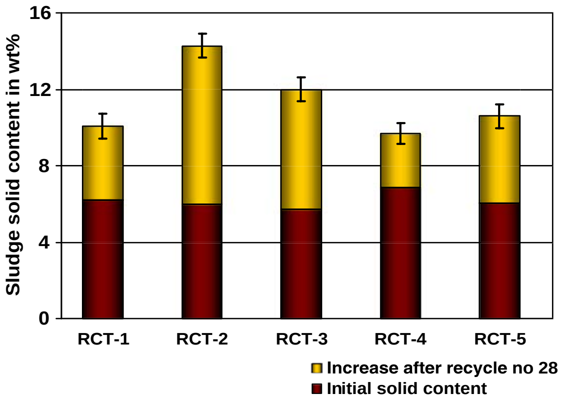

Fig. 5. Increase in sludge solid content from initial neutralization to final recycle step for RCT-series.

The pH profiles in the neutralizing tank during lime addition are given in Fig. 9. Looking at the distribution (in mole fractions) of monomeric iron hydrolysis products in equilibrium with amorphous hydroxides as a function of pH (Duan and Gregory, 2003), most of the species exist as $Fe(OH)^{2+}$ and Fe^{3+} at pH<2.7, while the concentration of $Fe(OH)_2^+$ becomes more significant at higher pH with continuing hydrolysis. In the first 20 minutes of lime addition, the pH in RCT-2 rose to 4.7, indicating that $Fe(OH)^{2+}$ was the major species present. On the other hand, the presence of $Fe(OH)^{2+}$ was more significant in RCT-1 as the pH stayed below 3.5 for the same period of time. It was thought that the presence of $Fe(OH)^{2+}$ would be more beneficial for the precipitation of hydroxides on the surface of existing sludge particles due to the higher positive charge (Ranich et al., 1993). However, the solid content and average particle size for RCT-2 implied that $Fe(OH)_2^+$ might be an important factor in encouraging larger and denser particles/agglomerates formation. Jamieson et al. (2003) observed the formation of fast-settling iron(III) precipitates at room temperature in the presence of sulphate ions, with ratio of Fe^{3+}/SO_4^{2-}~1:1 and total concentration <0.2 M, where $Fe(SO_4)^+$ was the dominant species. The conditions also favoured the generation of dense amorphous basic ferric sulphate particles (Flynn, 1984). It was proposed that $Fe(SO_4)^+$ complex possibly helped deter further polymerisation,

Table 4
The average volume mean diameter of sludge particles after initial neutralization and after 28 recycles for HDS, RCT, and CIC processes

Experiment	Average particle diameter (μm) after initial neutralisation	Average particle diameter (μm) after 28 recycles
HDS-1	39.3±1.8	46.6±2.0
HDS-2	39.2±1.9	42.2±4.4
HDS-3	23.7±0.4	73.2±1.2
RCT-1	37.6±1.0	33.6±0.8
RCT-2	37.7±0.3	118.5±3.0
RCT-3	54.2±1.2	21.7±0.1
RCT-4	43.0±0.1	17.7±1.0
RCT-5	43.0±1.1	20.5±0.3
CIC	45.0±0.5	45.1±0.4

promoted crystal growth, and aligned the iron atoms for a more ordered ferrihydrite or amorphous ferric sulfate to be formed on the surface of dissolving alkali reagents or recycled solids; therefore producing high density sediments (Jamieson et al., 2003). A similar phenomenon could occur in this case, where the presence of $Fe(OH)_2^+$ was more conducive than $Fe(OH)^{2+}$ for enlargement of existing solids. Further studies are currently being conducted to confirm and understand the role of different Fe(III) species in iron precipitation.

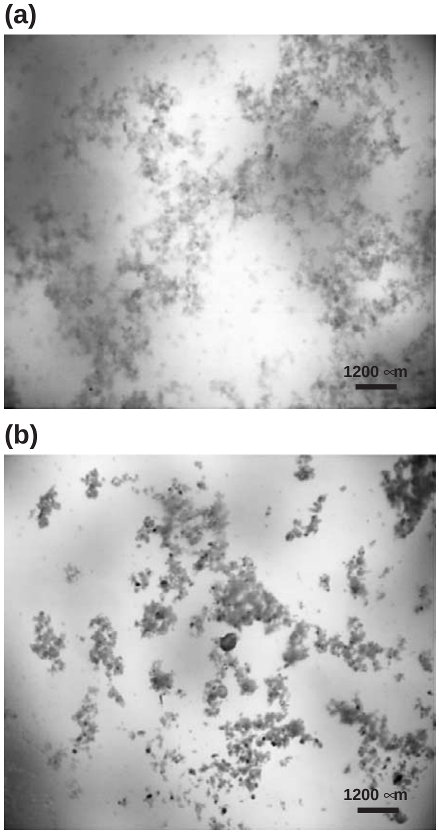

Fig. 6. Iron (III) hydroxide precipitates in suspension from HDS-3 after (a) 4 recycles and (b) 28 recycles.

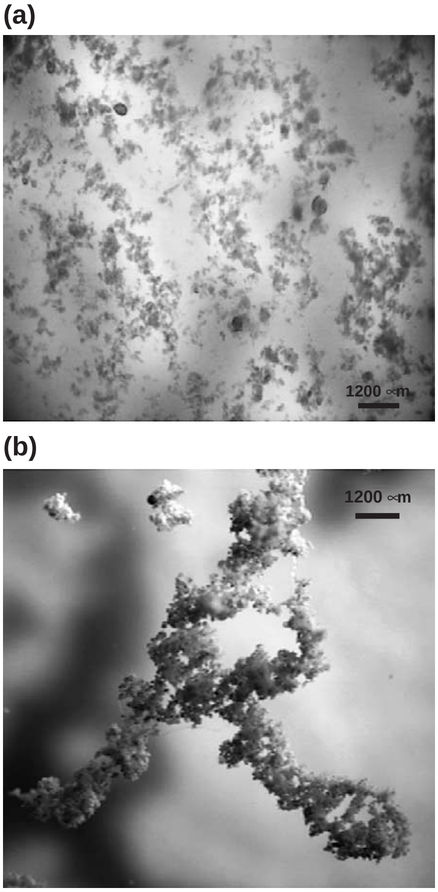

Fig. 7. Iron (III) hydroxide precipitates in suspension from RCT-2 after (a) 4 recycles and (b) 28 recycles.

A gradual pH change over the lime addition period allowed iron monomers/dimers to be properly formed and attached to the sludge particles, rather than being stripped back to the bulk solution to precipitate when there was an instantaneous increase in pH. By dosing the lime instantaneously as in RCT-4, the pH jumped from an initial value of 2.45 to pH 6 within 5 min. This was not an efficient dosing method, as it was found that the amount of lime required to raise the pH was approximately 15% higher compared to the other runs. The single dosing procedure reduces the efficiency of lime consumption due to the time required for lime to react. Nevertheless, it is often impossible for continuous operation in practice to subject a process to incremental changes in pH, as the level usually remains constant for each unit operation. Dosing the lime in 2-stages is potentially a more feasible option. In RCT-5, the pH was kept at <3 for the 1st stage and then increased to 6 in the 2nd stage, which improved the final solid content compared to the single-stage fast addition process, although it was not as high as RCT-2. Based on these findings, a prolonged mixing of recycled sludge and Fe(III) ions at the correct pH value, possibly between 3.5 and 4.5, could be the key to a better performance.

A TEM photograph from A-3 (Fig. 10(a)) shows small precipitates with distinctively needle-like structures. This type of configuration tends to have extensive interstitial water trapped between the pores, consequently producing sludges of relatively low density that have to be dewatered through mechanical means, such as centrifugation or filter press. Small agglomerates with few visible needle-shaped structures were also found in RCT-1 (Fig. 10(b)), possibly as a result of spontaneous precipitation when the pH suddenly increased from 3.5 to 5 after 20 min of lime addition, rather than by enlargement of existing solids.

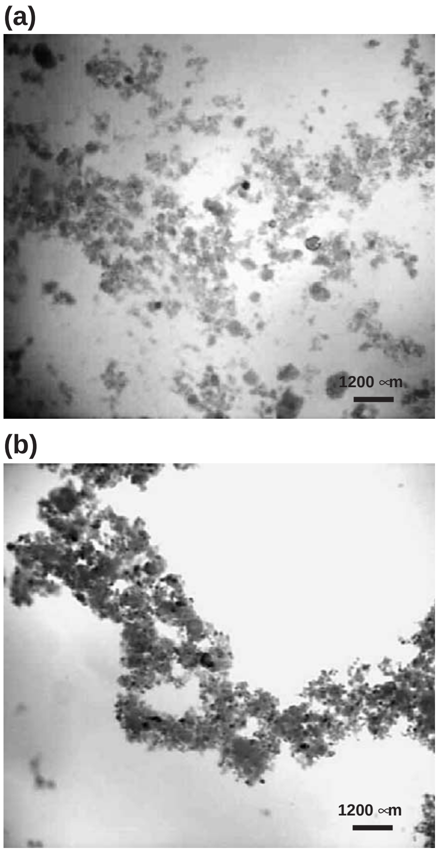

Fig. 8. Iron (III) hydroxide precipitates in suspension from CIC after (a) 4 recycles and (b) 28 recycles.

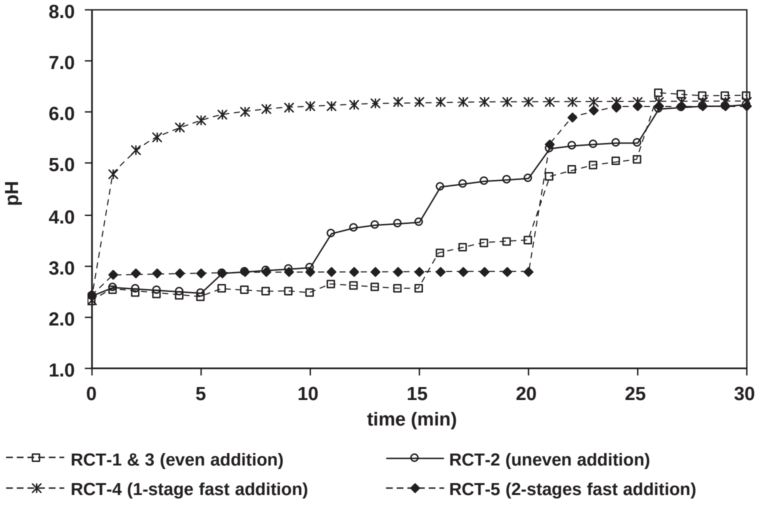

Fig. 9. pH profiles in the neutralizing tank for RCT-series.

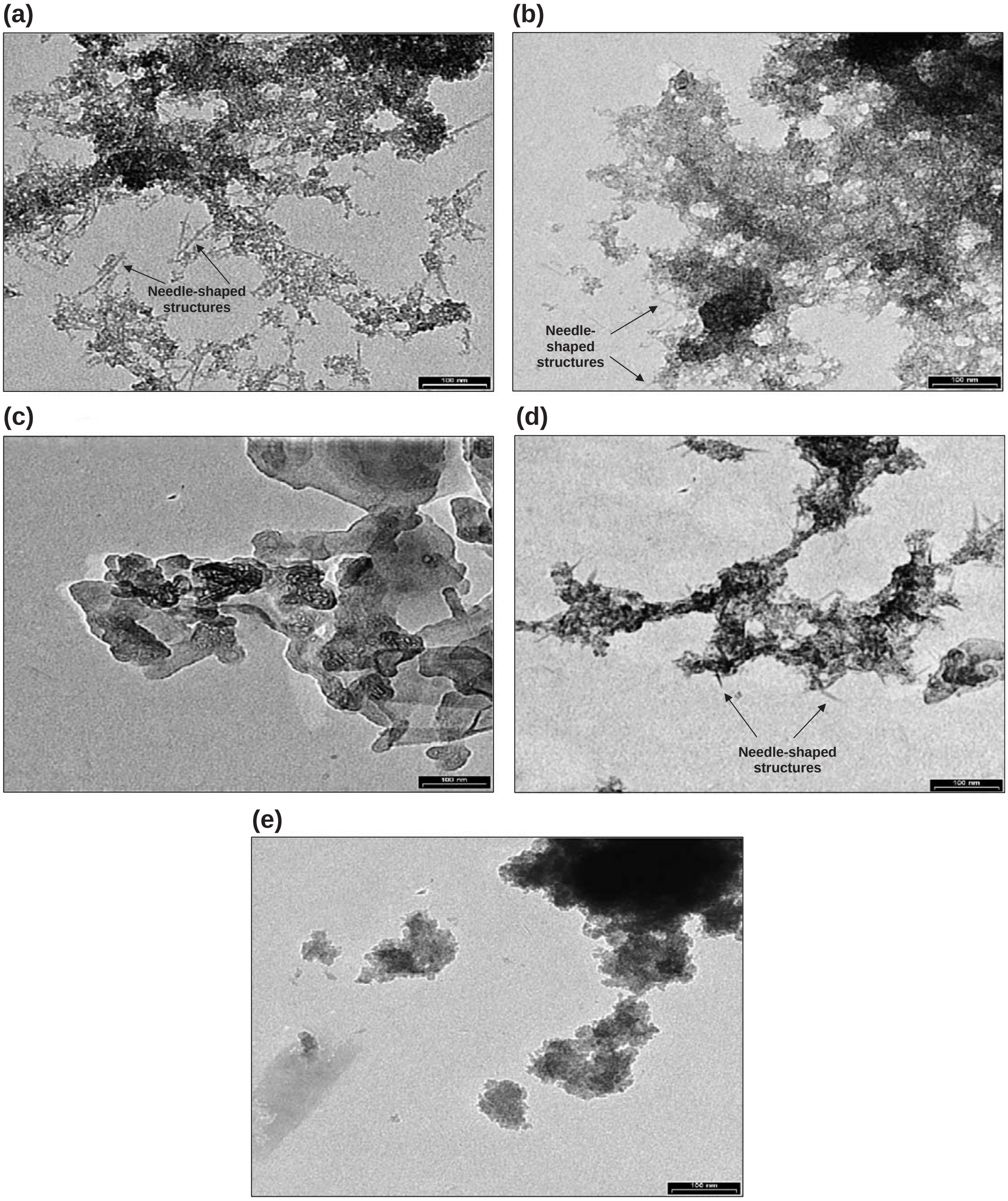

Fig. 10. TEM pictures of precipitates from (a) HDS-3, (b) RCT-1, (c) RCT-2, (d) RCT-4, and (e) CIC.

Larger precipitates with stacked, plate-like configurations were observed in RCT-2 (Fig. 10(c)). The transformation from initially rod-shaped (001) akaganeite particles to rafts consisting of similar-sized rods was observed to occur in a study on forced hydrolysis of ferric chloride solutions to synthesize iron oxide (Bailey et al., 1993). The formation of rafts was possibly caused by an ordered aggregation with weak magnetic moments aligning the rods of equal lengths. Hence, it indicates further particle growth or agglomeration in RCT-2 compared to HDS-3 or RCT-1, and has probably contributed to the increase in sludge density. This type of structure is more susceptible to densification during stirring or raking that expulses free water, and therefore is easier to be compacted. Needle-shaped solid structures were observed for RCT-4, possibly due to fast precipitation in bulk solution, rather than growth on solid surface (Fig. 10(d)), while small, irregular precipitates were observed for CIC (Fig. 10(e)).

XRD data of precipitates dried at 60 °C from RCT-2 and HDS-3, sampled at recycle number 4 and 28 denote that akaganeite was the main iron oxyhydroxide species (Fig. 11). The spectra were quite weak for both samples, indicating poor crystalline structures, while the crystallite size was smaller for

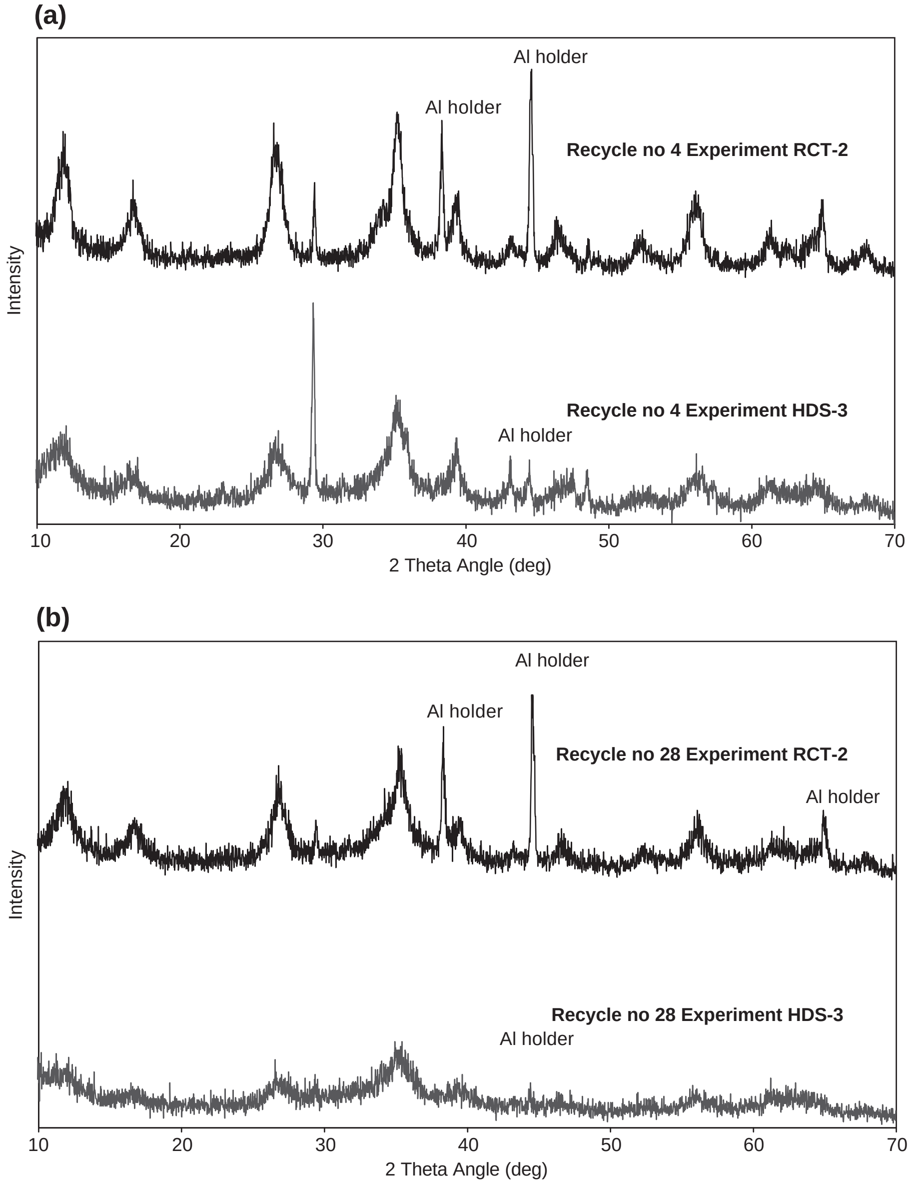

Fig. 11. XRD for dried precipitates from RCT-2 and HDS-3 at (a) recycle no. 4 and (b) recycle no. 28.

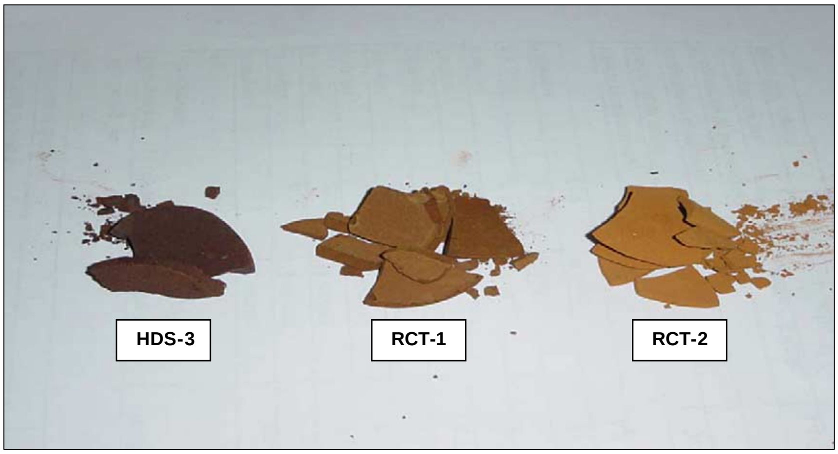

Fig. 12. Air-dried sludge from experiments HDS-3, RCT-1, and RCT-2.

HDS-3 compared to RCT-2 at the end of the recycles, as shown by the broader peaks. The colour of sludge from HDS-3 was much darker than those from either RCT-1 or RCT-2 (Fig. 12). This distinction in colour was presumably due to the size and shape of particles or agglomerates composing the sludge, rather than difference in the crystalline structure or ferric species.

5. Conclusions

Experiments were carried out to observe the parameters influencing the density of sludge formed in iron hydroxide precipitation. A slow precipitation rate and the presence of seed particles are beneficial for the generation of larger and denser agglomerates. The sludge density can be improved by adjusting the environment in which the reaction occurs. For iron hydroxide precipitation from the neutralization of iron chloride, the method of alkali addition was found to be a factor for improving sludge density. A prolonged mixing of existing solids and Fe(III) ions at specific pH environment favoured the growth of precipitates, while a sudden change in pH was detrimental to it. Accordingly, injecting the alkali slurry in unequal proportions was observed to be more effective than other dosing methods. In a continuous process, this may be achieved by conducting the neutralization in several stages. Precipitates with plate-like structures were produced under this condition, and were of higher density than needle-like precipitates formed under less effective dosing procedures. Flocculant addition helped creating stronger aggregates that could withstand stirring without significant size reduction. Nevertheless, the generated sludge tended to be more voluminous than those comprised of smaller particles/agglomerates.

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