

The Effect of Aluminium Source and Sludge Recycling on the Properties of Ettringite Formed During Water Treatment

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ABSTRACT

A range of techniques are available for the removal of sulfate ions from mine waters and industrial effluents. A number of processes involve the removal of sulfate as ettringite, a calcium aluminium sulfate ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) at elevated pH (11.5 – 13). Various process configurations have been proposed using lime and a source of aluminium to react with the sulfate in the process feed. This paper presents a study of the effect of the source of aluminium (when mixed with lime and synthetic sodium sulfate rich effluent) on the physicochemical properties of the resultant ettringite sludge and on the propensity of the precipitate, when recirculated, to form high density sludge (HDS). The study demonstrates that sodium aluminate (NaAlO_2), aluminium chloride (AlCl_3), aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) and polyaluminium chloride (PAC) all form ettringite and remove sulfate, with AlCl_3 being the most successful during 'single-pass' treatment. Furthermore, synthetic $\text{Al}(\text{OH})_3$ was demonstrated to be unreactive and the study also confirms the results of earlier literature that crystalline gibbsite does not form ettringite. The continuous trial with NaAlO_2 suggests that recirculation of sludge does improve the reaction kinetics of ettringite precipitation with lower residual sulfate concentrations being reached in similar residence time in the reaction tank when influent water is contacted with recirculated sludge. Different aluminium sources play a key role in determining the resultant sludge volume with NaAlO_2 forming a voluminous sludge and AlCl_3 -derived ettringite forming a denser single-pass sludge. Both reagents show only a slight tendency to form HDS upon recirculation. Microscopy images show differences in the precipitate morphology between Al sources and recycled precipitates. These results highlight the importance of understanding how reagent choice influences the properties of the resultant sludge properties, with the commensurate implications for process design, when applying the ettringite precipitation process for the removal of sulfate from effluents.

Keywords: Sulfate removal; high density sludge (HDS); sodium aluminate

INTRODUCTION

Elevated concentrations of the sulfate ion ($\text{SO}_4^{2-(\text{aq})}$) occur in water bodies impacted by acid mine drainage (AMD). The sulfate results from oxidation of the sulfur moiety of pyrite. Elevated sulfate concentrations are also common in other industrial effluents from smelting operations, pulp and paper mills, textile mills and tanneries (Galiana-Aleixandre et al. 2005; GBC 2000). Sulfate in itself is not toxic to humans. The taste threshold depends on the form in which the sulfate is present, but generally lies between 250 mg/L and 1000 mg/L. No health related issues have been reported or fully proven to be the result of any sulfate concentration and in terms of water quality standards no target have been set by WHO although their recommendation lies at 250 mg/L due to taste (WHO 2011). At concentrations greater than about 500 mg/L sulfate becomes a concern if the water contacts concrete infrastructure because it can cause deterioration of concrete, this can restrict disposal of sulfate-rich effluent to sewers.

The treatment of sulfate has for a long time been of secondary importance in water treatment due to the relatively low toxicity of sulfate compared to other contaminants. However, in the recent years environmental regulators have become more concerned with high sulfate concentrations in effluents especially when it is a key contributor to high total dissolved solids which are becoming a target of more stringent regulation. According to the International Network for Acid Prevention (INAP) it is therefore likely more demanding regulations will appear in the future (Lorax 2003). A number of treatment approaches for treating sulfate rich water have been variously reviewed in the literature (e.g. Bowell, 2004; Lorax, 2003). Some methods, in particularly those used for AMD, are developed to also clean water from metals and reduce the acidity. The existing methods can be broken down into four types (Lorax 2003) (i) Chemical treatment with mineral precipitation (ii) Membranes (iii) Ion exchange and (iv) Biological treatment. Note that ultimately membrane processes result in a concentrated sulfate brine which will require precipitation or crystallisation to produce a solid for final disposal. Biological processes generally rely on conversion by reduction to H_2S and either removed as metal sulphide or zero valent sulphur. Chemical treatments involve precipitation of the insoluble/sparingly soluble sulfate salts including gypsum, ettringite, barium sulfate (e.g. Bosman et al. 1990.), and jarosite. The Lorax(2003) report highlights ettringite precipitation processes as being particularly promising. The reaction occurs at elevated pH and involves reaction of dissolved sulfate with a source of aluminium (Al) and calcium (Ca) such that ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) precipitates. This paper concerns the ettringite precipitates that form during water treatment for the removal of sulfate.

Properties of ettringite precipitates

Ettringite can refer to both the mineral and the ettringite crystal structure (Tishmack and Burns 2004; Damons and Petersen 2002). The distinguishable features of the ettringite crystal structure are parallel columns comprising Ca^{2+} , Al^{3+} and OH^- structured units of $[\text{Ca}_6\text{Al}_2(\text{OH})_{12}\cdot 24\text{H}_2\text{O}]^{6+}$. Between the columns channels are formed where water is present as well as sulfate ions which balance out the structural charge (Johnson, 2004; Damons and Petersen 2002). The mineral can exchange some of its ions without adverse structural change (Damons and Petersen 2002). The actual water content of ettringite can change (24-32 moles per mole of ettringite) and a change in water content does

have an impact on the XRD peaks. (Tishmack and Burns 2004). Most research on ettringite is in conjunction with concrete where it is a common constituent phase. Much literature is focused on secondary ettringite formation which can be problematic due to growth and expansion of the mineral which causes cracking. A comprehensive study by Cody et al. (2004) investigated how the nucleation and growth of the ettringite crystals were affected by different chemicals. The findings from the study showed that different precipitate morphologies were found and were dependent on the type and amount of additives.

Although there are some publications covering the effectiveness of different reagents in removing sulfate by ettringite precipitation (e.g. Janneck et al, 2012), there is an absence of studies looking at the influence on the resultant sludge. This study came about after initial continuous trials of an ettringite precipitation process (detailed below) resulted in excessive volumes of precipitate, as compared to other mine water sludges that the authors are familiar with. This paper thus aimed to examine (i) the influence of aluminium source on the properties of the resultant sludge and (ii) to examine whether recirculation of the sludge leads to a densification of the final sludge. Sludge recirculation is well established in the High Density Sludge (HDS) process used commonly for the removal of metals from AMD (add reference). Recirculation of the sludge results in denser HDS (in terms of m/v) than single-pass sludge with better settling rates, dewaterability and reduced resistance to filtration which equates to better process economics (Coulton et al 2004). Among the published ettringite based sulfate removal processes, those of Outotec and Veolia incorporate sludge recirculation. Note that sludge recirculation is included in the SAVMIN process but only after regeneration of the sludge to active $\text{Al}(\text{OH})_3$ so this process is not comparable with that presented here.

METHODOLOGY

Initial Continuous Trial of Sodium Aluminate

The initial experiment began with a continuous pilot plant trial using sodium aluminate (NaAlO_2), based upon early trials showing that NaAlO_2 was a suitable source of soluble aluminium for ettringite precipitation. The pilot plant was supplied by G.U.N.T. Gerätebau GmbH. A photograph of the plant in use with NaAlO_2 and lime and a close-up of the ettringite precipitates can be seen in Figures 1 and 2. The plant consists essentially of a raw water tank, a reactor tank followed by a flocculation/coagulation train with up-and-over weirs, followed by a lamella clarifier. Reagents are dosed from reagent containers with feed pumps. Manual setting of the lime flow to the reactor tank was performed with regular pH measurements with a portable instrument. A sludge recirculation pump was installed and for most of the work up to two lime slurry feed pumps were installed. All chemical analyses were performed using the portable Hach Spectrophotometer following standard procedures (add reference).

The plant was configured to add lime and NaAlO_2 concurrently into the cylindrical precipitation vessel, where recirculated sludge was also added. Raw water feed rate was fixed initially at 10 litres per hour, giving a nominal residence time in the vessel of 1 hour excluding the influence of the thickened sludge re-circulation. Lime was added as a 5% m/v suspension to maintain the pH at the required value in the precipitation tank ($\text{pH} > 11.5$) and NaAlO_2 was dosed as a solution at 5 % m/v based on the stoichiometric amount of Al required. Anionic flocculant (NA 120 L) was dosed as an aqueous solution at a concentration of 0.005 % m/v to give a dosage between 1.3 and 2.6 mg/l of

dry polymer. Recirculation of sludge was achieved with the peristaltic pump (yellow in colour on Figure 1).



Figure 1. Photograph of plant in operation showing the ettringite precipitate in the clarifier and the external sludge recirculation pump in the foreground



Figure 2. Close-up of the clarifier with subdued lighting showing ettringite precipitates and clear overflow

Batch testing of different aluminium sources

The batch experiments treated a sodium sulfate solution by addition of stoichiometric quantities of aluminium (in various forms) and a 10 % stoichiometric excess of lime. The solution was kept at $SO_4 = 1500$ mg/L to avoid precipitation of gypsum. The chemicals used were 2.22 % m/v Na_2SO_4 solution, 5% m/v $Ca(OH)_2$ slurry, and the aluminium sources trialed were as follows: 25 % $AlCl_3 \cdot 6H_2O$, $NaAlO_2$, polyaluminium chloride (10% m/v), 22 % (m/v) $Al(NO_3)_3 \cdot 9H_2O$, aluminium hydroxide powder and synthesised aluminium hydroxide. The synthesised aluminium hydroxide was produced by neutralising 250 ml of a 2 % m/v $AlCl_3$ solution with NaOH. This resulted in a gel which was filtered, rinsed and dried.

Batch tests were carried out as follows: 100 ml of the Na_2SO_4 feed solution was added to a beaker placed on a magnetic stirrer. Reactions were started by introduction of 4 ml of the $Ca(OH)_2$ slurry. This was followed by aluminium addition (in which ever form). Immediately afterwards an additional 1.1 ml of the $Ca(OH)_2$ was added to the beaker. The suspension was allowed to stir for a total of 15 minutes. The suspension was then placed in a settling cylinder and the sludge allowed to settle for 15 minutes and then sludge volume recorded. This was the end point for 'single pass' experiments. For all non-final cycle (i.e. where the sludge was to be recycled) experiments, at the end of settling the supernatant was carefully decanted off and the sludge returned to the reaction beaker. 100 ml of Na_2SO_4 feed solution was added to the sludge in the reaction beaker and the next cycle begun. The experiments were thereafter repeated according to this procedure for between 1

and 12 cycles for AlCl_3 and 6 cycles for NaAlO_2 . To obtain images of the precipitate morphology 0.5 ml of suspension was removed during the 14th minute of the final cycle for recycled sludge experiments. The sample was spread across a petri dish and immediately oven-dried at 35°C prior to imaging under an optical microscope. At the end of all experiments solids were recovered by filtration, oven-dried at 35°C (for 24 hours) and weighed.

RESULTS AND DISCUSSION

Continuous pilot plant trial with sodium aluminate

Operation in this mode proved to be extremely challenging and in hindsight it would have been prudent to perform bench-scale batch tests (as was done for the remainder of the study) to determine whether sludge recirculation lead to densification of the ettringite sludge. It soon became impractical to return the thickened sludge to the precipitation tank using the peristaltic pump alone. For that reason it became necessary to employ a laborious method of filtering the sludge in a large Buchner funnel arrangement and return solids as a much thicker paste than was possible using the plant thickener. Nevertheless it was possible to keep running for about three weeks, treating about 800 litres of raw water containing up to 2350 mg/l of sulfate.

Figure 3 depicts the reduction in sulfate concentrations achieved throughout the pilot plant operation with NaAlO_2 as the source of Al and shows that a substantial improvement in removal efficiency took place as plant operation proceeded. In order to explain this trend it is necessary to consider the variations in other parameters that took place. Of particular note are the changes in aluminium dosages and rise in solids concentration in the reactor as time progressed. The pH in the precipitation reactor was slowly increased over time but was always above the target value of about 11.5 for ettringite precipitation. The improved sulfate removal cannot be attributed directly to the increase in aluminate dosage that occurred at Day 8. NaAlO_2 dose was increased from 0.17 l/h to 0.34 l/h after day 8 and then reduced to 0.25 l/h for days 15–25. It is more valid to examine the influence of stoichiometric amounts of Al present in the reactor. Up to Day 8 the removal of sulfate ion was approximately 10,000 mg/h. The Al addition rate was 2.8 g/h, thus representing an approximate stoichiometric excess of 50 %. Between Days 8 and 15 the removal of sulfate ion increased to about 20,000 mg/h whilst the excess of Al stayed at about 50 %. After Day 15 it was possible to add Al at approximately stoichiometric amounts and achieve removals of sulfate of up to 22,000 mg/h. It is concluded that the improved performance in terms of increase in the sulfate removal kinetics (implied by lower sulfate concentrations for the residence time) is the result of adding recycled solids to the precipitation vessel. It is interesting to note that very little improvement in sulfate removal efficiency occurred after the solids concentration exceed about 2 % m/v (i.e. 20 g/l).

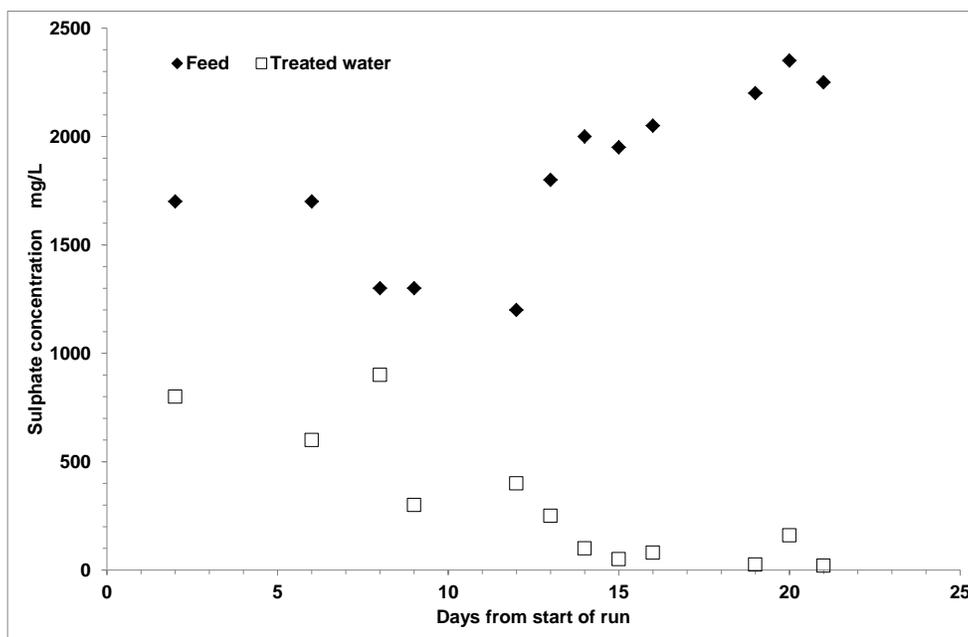


Fig 3. Variation in sulfate concentrations during pilot plant operation. pH > 11.5, Al dose variable (see text).

Batch trials with different aluminium reagents

In all cases where an obvious reaction occurred, the resultant precipitated solid was determined to be ettringite through XRD analyses. Furthermore ICP-OES on digested precipitates demonstrated the Ca, S, Al ratio expected for ettringite.

Initial Sludge Volumes

Table 1 shows the results of the single-pass ettringite precipitation experiments with various reagents providing the source of aluminium. Several important observations are as follows: In agreement with literature $\text{Al}(\text{OH})_3$ powder is found to be largely unreactive, synthetic $\text{Al}(\text{OH})_3$ was also found to be unreactive. AlCl_3 forms the least voluminous single pass sludge, and removes sulfate to the lowest residual level. The use of NaAlO_2 results in the most voluminous sludge (80 ml per 100 ml of influent treated) and relatively poor sulphate removal.

Propensity for sludge to densify during recycling

Figure 4 shows the effect of recycling the ettringite sludge on the resultant sludge volume where NaAlO_2 or AlCl_3 has been used as the Al source for ettringite precipitation. The 'predicted' sludge volumes are based on projections of sludge volume accumulating at the same volume that the single-pass sludge precipitated, and assuming incompressibility of the sludges. It can be seen that the initial trend of relatively high precipitant volume is observed to continue over 6 cycles for the

NaAlO₂ based sludge (in fact, the experiment had to be abandoned after 6 cycles due to impracticality of recycling the sludge). However, there is some evidence of sludge densification due to recycling of the sludge compared to projections based on single pass sludge volumes. Similarly, it can be again seen that AlCl₃ forms a much lower volume precipitate and that recycling of this precipitate leads to a slight densification over the volume of sludge expected from projection of the single-pass sludge volumes. However, beyond 9 cycles no further benefit is observed. These data indicate that sludge recycling confers some small benefits in terms of sludge densification as well as improved reaction kinetics.

Table 1 Mean residual sulfate and settled sludge volumes for different aluminium sources when precipitating ettringite from solutions with initial sulfate concentration = 1467 mg/L

Reagent	Number of experimental repeats	Mean Residual sulfate concentration (mg/L± stdv)	Settled sludge volume* (mL per 100ml of influent)
NaAlO ₂	3	525 (± 19.2)	80 (± 17)
AlCl ₃	4	365 (±193)	16 (± 2)
Al(NO ₃) ₃ ·9H ₂ O	2	383	28
PAC	3	639 (±263)	22 (±2)
Al(OH) ₃ powder	1	1269	94
Al(OH) ₃ synthetic	1	1464	95

*In 15 mins of settling time

Morphological characteristic of ettringite sludge

The optical microscopy reveals that the morphology of the ettringite precipitates varies for different Al source and also by recycling of the sludge. Figure 5 (a) and (b) show the NaAlO₂ single-pass and 6x recycled sludge. It can be seen that both the single pass sludge and the recycled sludge do not show the classical needle-like morphology of ettringite, but rather that small spherical particles dominate, this is particularly clear for the recycled sludge. Interestingly Cody et al. (2004) observed that large amounts of Na (added as NaCl) leads to the formation of spheres of ettringite precipitate rather than needles. Figure 5 (c) and (d) shows the AlCl₃ single-pass and 12x recycled sludge. The single-pass sludge demonstrates amorphous masses of crystals whereas the 12x recycled sludge shows that this early morphoogy has changed to a prounounced needle-like morphology (with needles of up to 100 µm) more typical of pure ettringite. It is clear that during recycling the precipitates have changed its morphology, whether this is due to ageing or through crystal growth is not known.

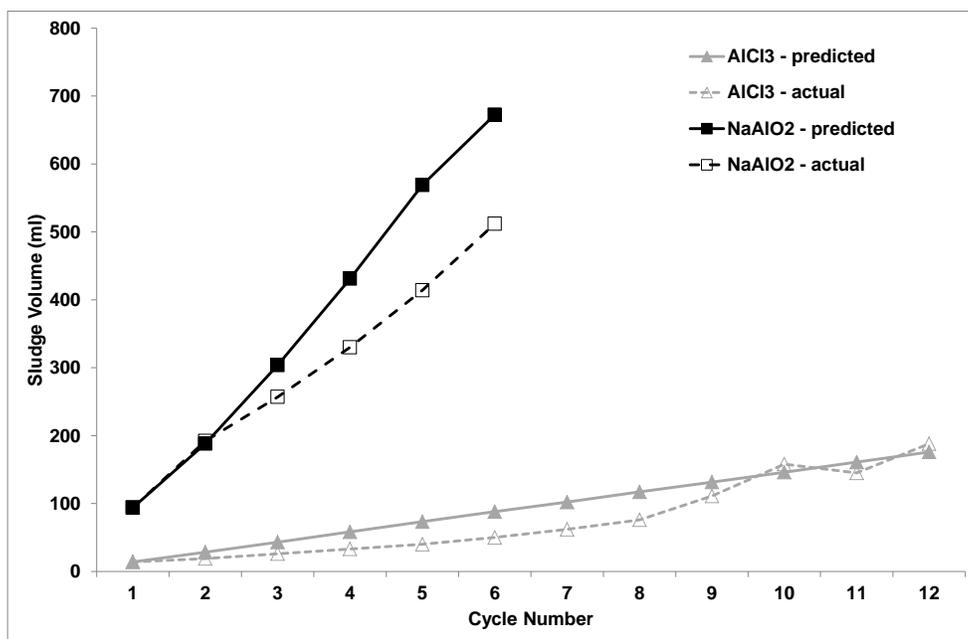


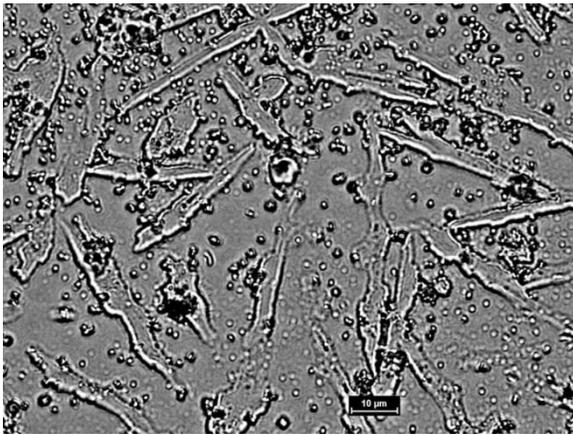
Fig 4. Effect of sludge recycling on volume of ettringite precipitation. Predicted volumes are based on projection of the single-pass sludge volume (corrected for measured sulfate removal)

Cody et al. (2004) describe how (i) nucleation of ettringite may be completely inhibited and another less stable mineral such as calcium aluminate monosulfate forms, (ii) how nucleation gel/colloid can form or nucleation (iii) or crystal growth can be inhibited and can affect growth in numerous ways depending on which crystal planes are poisoned by foreign ions. This study along with Cody et al. (2004) indicates that ettringite precipitates seem to be sensitive to the aqueous environment from which they form and that this can have profound effects on the nature of the sludge formed.

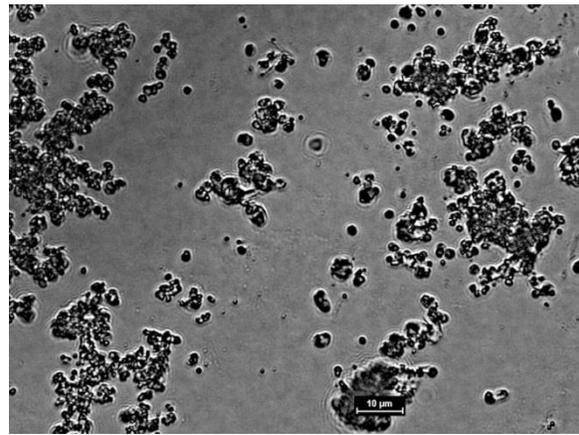
CONCLUSIONS

The following conclusions are drawn from this study:

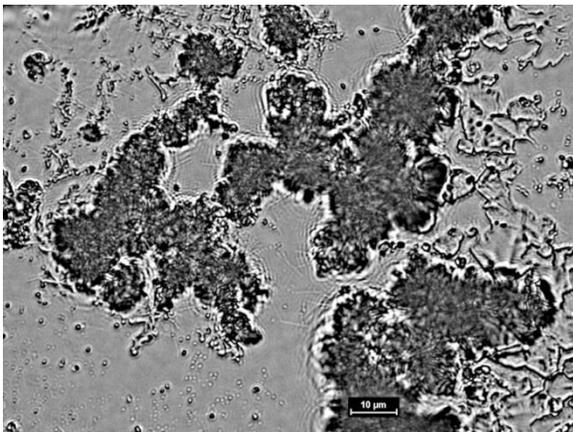
- Sodium aluminate produced a voluminous ettringite sludge during both continuous operation and batch testing relative to aluminium chloride
- Using aluminium chloride as the aluminium source leads to the lowest residual sulfate levels in single-pass operation.
- Recirculation of the sodium aluminate based sludges yielded improvements in sulfate removal, which in the context of the continuous operation equates to better removal process kinetics



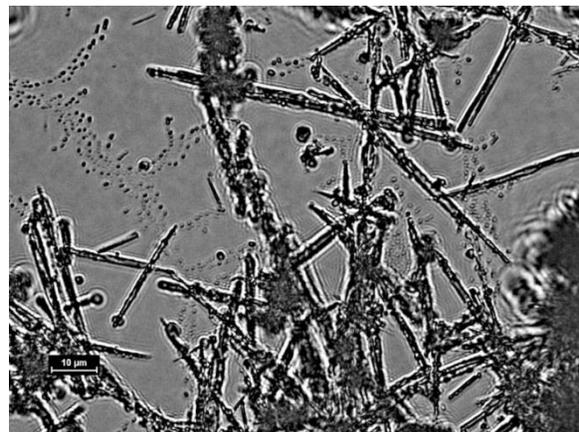
(a) NaAlO_2 single-pass sludge, 100 x magnification



(b) NaAlO_2 6 x recycled sludge, 100 x magnification



(c) AlCl_3 single-pass sludge, 100 x magnification



(d) AlCl_3 12 x recycled sludge, 100 x magnification

Fig 5. Optical mineralogy of air dried ettringite sludge.

- Recirculation of the sodium aluminate and aluminium chloride based sludges showed that the sludges have the propensity to slightly densify on recycling
- Morphological differences were observed between precipitates formed from different reagents and when recycled
- The choice of Al-bearing reagent will influence the morphology of the precipitate formed during the ettringite precipitation process, crucially these microscopic morphological changes correlate with macroscopic sludge characteristics.

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