

# Removal of sulfate ion from semiconductor wastewater by ettringite precipitation

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**Abstract.** This study seeks towards an optimal way to control sulfate ions in semiconductor wastewater effluent with potential eco-toxicity. We developed a system based on ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ). The basic idea is that the pH of the water is raised to approximately 12 with  $\text{Ca}(\text{OH})_2$ . After, aluminium salt is added, leading to the precipitation of ettringite. Lab-scale batch and continuous experiment results with real semiconductor wastewater demonstrated that 1.5 and 1 of stoichiometric quantities for  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  with pH above 12.7 could be considered as the optimal operation condition with 15% of sludge recycle to the influent. A mixed  $\text{AlCl}_3 + \text{Fe}$  reagent was selected as the beneficial  $\text{Al}^{3+}$  source in ettringite process, which resulted in 80% of sludge volume reduction and improved sludge dewaterability. The results of continuous experiment showed that with precipitation as ettringite, sulfate concentration can be stably reduced to less than 50 mg/L in effluent from the influent  $2,050 \pm 175$  mg/L on average (1,705 ~ 2,633 mg/L).

**Keywords:** eco-toxicity; ettringite; semiconductor wastewater; sludge volume reduction; sulfate ion;

## 1. Introduction

In recent years, hitherto-unregulated pollutants are of a serious concern under increasingly stringent water regulation, including micro-pollutants and ionic species such as sulfate ions ( $\text{SO}_4^{2-}$ ). Although environmental laws pay less attention to  $\text{SO}_4^{2-}$  than other pollutants such as organic compounds, nitrogen or heavy metals, the World Health Organization (WHO) places 250 mg/L guideline (as  $\text{Na}_2\text{SO}_4$ ) on  $\text{SO}_4^{2-}$  for drinking water. It was corroborated that highly concentrated  $\text{SO}_4^{2-}$  results in osmotic inhibition and witheredness of crops. There indeed have been occasional issues that the rice field near discharge points of  $\text{SO}_4^{2-}$  enriched industrial wastewater effluent was damaged, especially in winter season with limited precipitation in Monsoon climate. In addition, anaerobic reduction of  $\text{SO}_4^{2-}$  can also generate  $\text{H}_2\text{S}$  to bring about odor and sewer corrosion (Pikaar *et al.* 2017). The potential eco-hazard of  $\text{SO}_4^{2-}$  would pose a serious liability for the industry to necessitate a reliable  $\text{SO}_4^{2-}$  reduction processes. It is known that semiconductor wastewater effluent has a significantly higher sulfate ion concentration than sewage treatment effluent. As a result of the field investigation, it was confirmed that the concentration of  $\text{SO}_4^{2-}$  in wastewater discharged from a typical semiconductor manufacturing plant was 1,700ppm or more on average, which greatly increased the concentration of  $\text{SO}_4^{2-}$  in rivers. The impacts of the effluent discharge would be intensified in winter season with lower precipitation depths in Monsoon climate area. Our goal is to develop a viable deionization system that can remove the sulfate ion concentration below 250

ppm, which is the drinking water quality standard.

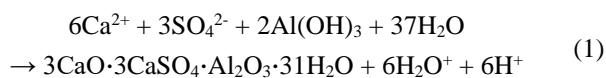
The  $\text{SO}_4^{2-}$  removal can be realized by biological treatment, membrane filtration, ion exchange/adsorption, evaporation/crystallization and chemical precipitation (e.g., gypsum and ettringite) (Nguyen *et al.* 2021, Dou *et al.* 2017, Howell 2004, Işık Kabdaşlı *et al.* 2016, Bertolino *et al.* 2011, Silva *et al.* 2010). The biological  $\text{SO}_4^{2-}$  reduction to  $\text{S}^2/\text{S}^0$  by sulfate reducing bacteria has some disadvantages, including slow process kinetics, requirements of large installation area, inhibition by relatively high salinity and metals ions, and generation of hydrogen sulfide that is another toxic compound (Dou *et al.* 2017). In comparison, physico-chemical technologies, including ion exchange, capacitive deionization, electro dialysis and reverse osmosis, could be more effective for  $\text{SO}_4^{2-}$  removal. However, the investment and operating costs are relatively high to limit a full-scale application. Moreover, the high concentration and large volumes of liquid waste (brine water) would require additional treatment and disposal costs (Dou *et al.* 2017, Guo *et al.* 2018). Therefore, development of the next-generation  $\text{SO}_4^{2-}$  removal technology was necessary to reduce the overall cost for installation, operation, and land requirement. The necessary conditions for an optimal sulfate removal process include i) minimum dosage of chemicals which increase the level of counter ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), ii) selective separation of  $\text{SO}_4^{2-}$ , and iii) control and conversion of brine water into solid waste.

Conventionally, lime based precipitation reduces  $\text{SO}_4^{2-}$  concentrations through the precipitation of gypsum ( $\text{CaSO}_4$ ). Because gypsum is slightly soluble in water ( $K_{sp} = 3.14 \times 10^{-5}$ ), both theoretical calculations and field results showed greater than 2,000 mg/L of calcium would remain dissolved in effluent after the gypsum precipitation. In addition, the gypsum precipitation by itself is not sufficient to meet the 250 ppm as  $\text{SO}_4^{2-}$  of the WHO drinking water quality

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standard. (Pikaar *et al.* 2014, Bertolino *et al.* 2011). Owing to far lower solubility than  $\text{CaSO}_4$ , ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ,  $K_{sp} = 3.14 \times 10^{-45}$ ) could enhance the high pH lime-based precipitation, and has been considered as a promising way for  $\text{SO}_4^{2-}$  removal. The studies of ettringite precipitation were considered successful with several types of industrial wastewaters, such as, textile (Kabdasli *et al.* 2015), mine water (Tolonen *et al.* 2016), leachate from municipal landfill (Aygün *et al.* 2018), and lignite coal mining (Norapat *et al.* 2021), achieving sulfate removal above 85%. In particular, the ettringite based coagulation could fit to the semiconductor wastewater treatment, since the lime dose brought about a concurrent reduction in fluoride concentrations in the effluent. Nevertheless, there is a lack of literature on the ettringite precipitation process for real semiconductor wastewater treatment.

An ideal ettringite precipitation reaction is given by the following reaction (Hampsoim *et al.* 1982):



The model crystal structure of ettringite is illustrated in Fig. 1. The parallel columns consist of  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{OH}^-$  structured units of  $[\text{Ca}_6\text{Al}_2(\text{OH})_{12}\cdot 24\text{H}_2\text{O}]^{6+}$ . The channels between these columns are intercalated with  $\text{SO}_4^{2-}$  and water (Moore *et al.* 1968, Usinowicz *et al.* 2006). Theoretically, the ettringite process can reduce the sulfate concentration to less than 50 mg/L under a proper additions of lime and alumin(ifer)ous reagents.

In this research,  $\text{SO}_4^{2-}$  removal from real semiconductor wastewater by ettringite process was investigated in lab-scale batch and continuous reactors. The primary focus of this study was to evaluate the influence of operational parameters, including pH value, dosage of  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$ , source of aluminum and sludge recycling on the performance of ettringite process. The results obtained in this study are expected to provide an ettringite precipitation technology that can potentially be a feasible solution to treat semiconductor wastewater to meet the potential regulation (< 250 mg/L) and to identify important process parameters.

## 2. Materials and experimental methods

### 2.1 Source of wastewater

Semiconductor wastewater used in this study was taken from a semiconductor fabrication facility in South Korea. The main characteristics of semiconductor wastewater were as follows: pH of 1.37~3.26, ORP of 694 mV,  $\text{NH}_3\text{-N}$  of 327 mg/L, T-N of 376 mg/L, T-P of 114 mg/L, TKN of 327 mg/L,  $\text{NO}_3\text{-N}$  of 33mg/L,  $\text{SO}_4^{2-}$  of 1,798 mg/L, F<sup>-</sup> of 616 mg/L, Cl<sup>-</sup> of 264 mg/L,  $\text{PO}_4^{3-}\text{-P}$  of 114 mg/L,  $\text{Al}^{3+}$  of 0.4 mg/L,  $\text{Ca}^{2+}$  of 115 mg/L,  $\text{Mg}^{2+}$  of 7.8 mg/L,  $\text{Na}^+$  of 586 mg/L,  $\text{Fe}^{2+}$  of 0.4 mg/L,  $\text{Cu}^{2+}$  of 0.2mg/L,  $\text{Mn}^{2+}$  of 0.4 mg/L, Si of 15.5 mg/L and suspended solid (SS) of 69 mg/L, chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) of 570 mg/L, and conductivity of 6,904 mS/cm on average.

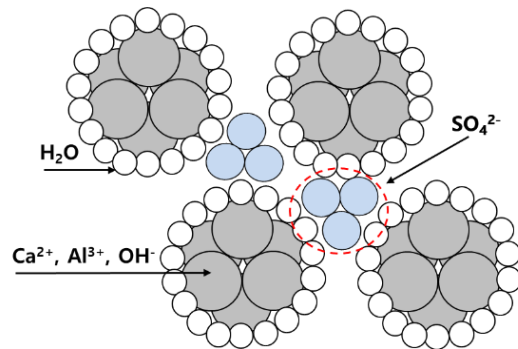


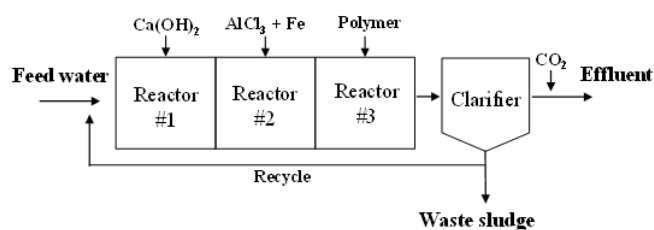
Fig. 1 Schematized ettringite structure

### 2.2 Lab-scale batch experiment

Batch experiments were performed using programmable paddle stirrer equipment at room temperature ( $25 \pm 0.5^\circ\text{C}$ ) for 500 mL wastewater sample in 1 L glass beaker. The three variables with the following levels were investigated; stoichiometric quantities of  $\text{Ca}^{2+}$  (0.5, 1.0, 1.5, 2.5) and  $\text{Al}^{3+}$  (0.75, 1.0, 2.2) together with pH (12.4 ~ 12.8). The sulfate removal efficiency was the response variable. The stoichiometric quantities (concentration) of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  were mostly adjusted by dissolving anhydrous  $\text{Ca}(\text{OH})_2$  and  $\text{NaAlO}_2$ , respectively. In selective experiments different sources of Al ( $\text{AlCl}_3$  and  $\text{AlCl}_3 + \text{Fe}$ ) were evaluated. The pH was adjusted by 6 mol/L NaOH solution and recorded by a portable meter (Hach, USA). The sample was mixed at 200 rpm for 70 minutes and then 10 ppm of polymer (anionic polyacrylamide) was added to the sample. Subsequently, a quiescent condition was allowed for sedimentation for 30 minutes. The supernatant was taken to determine concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and SS (suspended solids). The settled precipitates were washed thoroughly with deionized water to eliminate bound ions and dried in an oven at  $50^\circ\text{C}$  that would not change the nature of precipitates for solid analysis. In order to evaluate the influence of operating condition and chemical type on the formation of ettringite, the collected precipitates were interrogated with field emission scanning electron microscope (SEM, Nova) and X-ray diffraction (XRD, Dmax2500/PC). During the SEM analysis, a special attention was paid to the surface of the crystal to illustrate the precipitates microstructure. In addition, the main peaks obtained from XRD analysis were further compared to verify the conformance with a standard library for ettringite.

### 2.3 Lab-scale continuous experiment

The schematic diagram of continuous ettringite process (effective volume of 4 L) was illustrated in Figure 2. The process essentially consists of the following three steps: 1) Reactor #1: Addition of  $\text{Ca}^{2+}$  for initial precipitation of  $\text{SO}_4^{2-}$  as gypsum and the increase of pH, 2) Reactor #2: Addition of  $\text{Al}^{3+}$  for precipitation of  $\text{SO}_4^{2-}$  as ettringite, 3) Reactor #3: Addition of polymer for ettringite flocculation. In particular, the bulk pH in reactor #1 was adjusted to > 12.7 using 0.2 M  $\text{Ca}(\text{OH})_2$  solutions. The final effluent produced from a clarifier for precipitation underwent a pH



(a)



(b)

Fig. 2 Schematic representation of the ettringite precipitation process (a) and picture for the lab-scale apparatus (b)

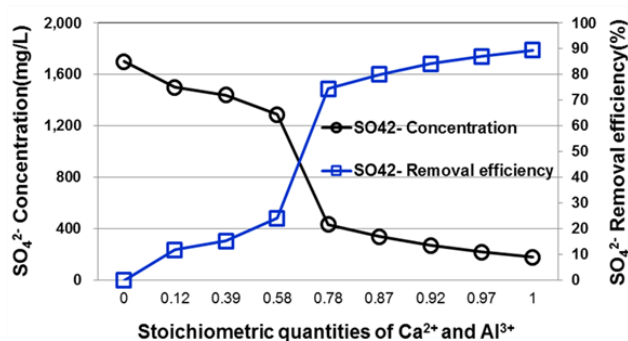


Fig. 3 The variation of SO<sub>4</sub><sup>2-</sup> concentration and removal efficiency at different stoichiometric quantities of Ca<sup>2+</sup> and Al<sup>3+</sup>

adjustment and residual Ca<sup>2+</sup> removal steps using CO<sub>2</sub> gas bubbling. In selected experiments, a portion of the ettringite sludge from the clarifier was recycled and mixed with the feed water in the reactor #1.

#### 2.4 Analysis

The pH and temperature of the samples were measured using a F-71G pH meter (HORIBA, Japan). The concentrations of Ca<sup>2+</sup> and Al<sup>3+</sup> were determined using the ICP-7510 (Shimadzu, Japan) and other analysis e in accordance with *Standard Methods for the Examination of Water and Wastewater* (Baird 2012). Concentrations of anions were measured with ion chromatograph (IC) device (Dionex, USA). The precipitated solids were analyzed by X-ray diffraction (XRD) was performed by D8 Advance diffractometer (Bruker, United States), using a CuK $\alpha$  tube with  $\lambda = 1.545 \text{ \AA}$  as the X-ray source to study the phase formation and transformation of ettringite precipitates. The elemental composition and morphology of the composite materials were analyzed using Scanning electron

microscopy (SEM) (FE-Scanning Electron Microscope, JEOL JSM 6335 F, Japan) with an energy-dispersive X-ray spectroscopy (EDS).

### 3. Result and discussion

#### 3.1 Effects of Ca<sup>2+</sup> and Al<sup>3+</sup> doses on SO<sub>4</sub><sup>2-</sup> removal from semiconductor wastewater

Wastewater with the initial SO<sub>4</sub><sup>2-</sup> concentration of 1,722 mg/L was treated with variable Ca<sup>2+</sup> and Al<sup>3+</sup> dosages under controlled pH at 12.5 and retention time of 100 minutes.

Fig. 3 displays that the removal efficiency of SO<sub>4</sub><sup>2-</sup> gradually increased with Ca<sup>2+</sup> and Al<sup>3+</sup> dosage from 0 to 1 of stoichiometric quantities. The maximum removal efficiency of 89% was obtained, at the stoichiometric quantities of Ca<sup>2+</sup> and Al<sup>3+</sup> dosage. The loss in efficiency would be ascribed to competing reactions, namely co-precipitation of CaCO<sub>3</sub>, Ca<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)(OH)<sub>12</sub>, CaF<sub>2</sub>, CaSO<sub>4</sub>, Al(OH)<sub>3</sub> as impurities of the ettringite. On the other hand, the dependency of SO<sub>4</sub><sup>2-</sup> removal on the doses of Ca<sup>2+</sup> and Al<sup>3+</sup> was nonlinear; *i.e.*, the efficiency was sharply raised when the stoichiometric quantity increased from 0.58 to 0.78. The increase in Ca<sup>2+</sup> dosage led to increased generation of CaSO<sub>4</sub>, that is known to facilitate coagulation and adsorptive removal of SO<sub>4</sub><sup>2-</sup> (Usinowicz *et al.* 2006). In addition, the added Ca(OH)<sub>2</sub> partly increased pH, thus elevating the ettringite generation to improve SO<sub>4</sub><sup>2-</sup> removal (Dou *et al.* 2017). The pH would be a principal parameter that defines the stability of ettringite and the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in equilibrium (effluent).

In order to optimize the comprehensive effects of Al<sup>3+</sup>, Ca<sup>2+</sup> and pH on SO<sub>4</sub><sup>2-</sup> removal, wastewater with the initial SO<sub>4</sub><sup>2-</sup> concentration of 1,873 ppm was treated with various conditions, as shown in Table 1. At fixed stoichiometric dose of Al<sup>3+</sup> (Case 1), the SO<sub>4</sub><sup>2-</sup> removal efficiency was dramatically improved from 44.5% to 83.8% as the stoichiometric quantity of Ca<sup>2+</sup> was elevated from 0.5 to 1, in agreement with Figure 3. When the Ca<sup>2+</sup> dosage further increased in a stoichiometric excess of 50%, almost complete removal (98.7%) of SO<sub>4</sub><sup>2-</sup> was achieved. Evidences have been presented that stoichiometric quantity of 1.5 could be the optimum Ca<sup>2+</sup> dose for ettringite precipitation, ascribed to the scavenging reactions (Dou *et al.* 2017, Bertolino *et al.* 2011). In particular, an excess amount of calcium ions is required when fluoride ions are present in feed wastewater, due to the formation of calcium fluoride (CaF<sub>2</sub>) (Usinowicz *et al.* 2006). As readily expected, greater stoichiometric excess of 150% only slightly raised the removal efficiency near 99% in spite of the substantially incremented dose (cost) of chemicals.

At a given stoichiometric dose of Ca<sup>2+</sup> (Case 2), on the other hand, the removal efficiency of SO<sub>4</sub><sup>2-</sup> (42.3%) was also sharply elevated from 42.3% to 90.2% when the stoichiometric quantity of Al<sup>3+</sup> increased from 0.75 to 1. The imperfect removal at the theoretical Al<sup>3+</sup> input was in line with previous studies reporting that the optimum Al<sup>3+</sup> dosage should be slightly over-stoichiometric, owing to the other concurrent precipitates such as Al(OH)<sub>3</sub> (Dou *et al.* 2017, Kabdasli *et al.* 2011). Parallel formation of kuzelite

Table 1 Summary of lab-scale batch experiments at various operational conditions

Test volume: 500mL	Stoichiometric quantities of Al <sup>3+</sup>	Stoichiometric quantities of Ca <sup>2+</sup>	pH	Effluent			
				SO <sub>4</sub> <sup>2-</sup>		Al <sup>3+</sup>	Ca <sup>2+</sup>
				mg/L	Removal (%)	mg/L	mg/L
Case 1			1.37	1,873	-	1.6	112.0
Test 1-1	1.0	0.5	11.4	1,020	44.5	215.0	81.4
Test 1-2	1.0	1.0	12.4	303	83.8	71.3	21.7
Test 1-3	1.0	1.5	12.8	24.9	98.7	0.5	271.0
Test 1-4	1.0	2.5	12.8	11.7	99.4	0.4	453
Case 2			1.37	1,873	-	1.6	112
Test 2-1	0.75	1.0	12.7	1,080	42.3	-	-
Test 2-2	1.0	1.0	12.5	183.6	90.2	-	-
Test 2-3	2.2	1.0	12.5	954.0	49.1	-	-
Case 3			1.63	1,873	-	16.3	112
Test 3-1	1.0	1.5	12.4	303	83.8	-	21.7
Test 3-2	1.0	1.5	12.5	304	83.8	6.0	1.8
Test 3-3	1.0	1.5	12.6	154	91.8	6.2	1.2
Test 3-4	1.0	1.5	12.7	50.4	97.3	6.0	3.0
Test 3-5	1.0	1.5	12.8	11.8	99.4	5.9	135

(Ca<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)(OH)<sub>12</sub>) could require more Al<sup>3+</sup> dose than ettringite at a given SO<sub>4</sub><sup>2-</sup> concentration. Rather surprisingly, an excessive Al<sup>3+</sup> input (2.2 of stoichiometric quantity) significantly deteriorated the removal efficiency. This result might partly be ascribed to the concurrent addition of Na<sup>+</sup> cations. Owing to a lack of precipitation mechanism, the residual Na<sup>+</sup> could potentially elevate the effluent ionic strength and interfere with the ettringite solubility. More importantly, the increment in Al<sup>3+</sup> dose would facilitate a dominant formation of Al(OH)<sub>3</sub> that could bring about re-dissolution of ettringite. Therefore, the Ca<sup>2+</sup> and Al<sup>3+</sup> dosages at 1.5 and 1 of stoichiometric quantity were corroborated to be optimal and fixed for the further designed experiments under variable pH.

### 3.2 Effect of pH on SO<sub>4</sub><sup>2-</sup> removal from semiconductor wastewater

As shown in Case 3 (Table 1), with Ca<sup>2+</sup> and Al<sup>3+</sup> dosages fixed at 1.5 and 1 of stoichiometric quantities, there were considerable variations in the SO<sub>4</sub><sup>2-</sup> removal efficiency depending on the variations of pH within 12.4 ~ 12.8 range in the following orders: pH 12.8 (99.4%) > pH 12.7 (97.3%) > pH 12.6 (91.8%) > pH 12.5 (83.8%) ~ pH 12.4 (83.8%). The effluent SO<sub>4</sub><sup>2-</sup> concentrations significantly changed within such a narrow pH range, to support a dominant role of pH control in ettringite coagulation processes for SO<sub>4</sub><sup>2-</sup> removal. In other words, pH significantly affects the achievable level of effluent SO<sub>4</sub><sup>2-</sup> concentration. These results were in general agreement with the previous observations (Tait *et al.* 2009); ettringite can be stable at pH values > 10.7, but completely dissolves at near-neutral pH. In addition, the stability of ettringite formation depending on pH should be understood in association with precipitations

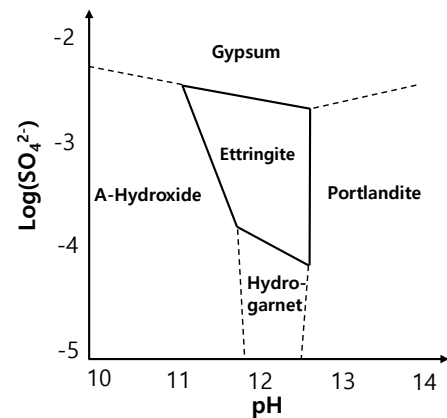


Fig. 4 Ettringite stability in alkaline environments (Hampsoim *et al.* 1982)

of gypsum (CaSO<sub>4</sub>) and aluminium hydroxide (Al(OH)<sub>3</sub>).

According to a previous report on log C-pH diagram for solids precipitation (Hampsoim *et al.* 1982), the ettringite precipitation requires specific ranges for pH and SO<sub>4</sub><sup>2-</sup> concentration. In particular, the competition between CaSO<sub>4</sub> and ettringite principally depends on the SO<sub>4</sub><sup>2-</sup> concentration, whereas pH more effectively alter the speciation between Al(OH)<sub>3</sub> and ettringite. Therefore, the strong sensitivity of SO<sub>4</sub><sup>2-</sup> removal on pH would be mostly associated with Al(OH)<sub>3</sub> rather than CaSO<sub>4</sub>, in agreement with the detrimental effects of excessive Al<sup>3+</sup> as above. Consequently, it could be concluded that 1.5 and 1 of stoichiometric quantities for Ca<sup>2+</sup> and Al<sup>3+</sup> at pH above pH near 12.8 were concluded as the suitable operation condition to maximize the SO<sub>4</sub><sup>2-</sup> removal (Germishuizen *et al.* 2018). A pH condition exceeding 13 was expected to hamper the ettringite precipitation by transition into portlandite

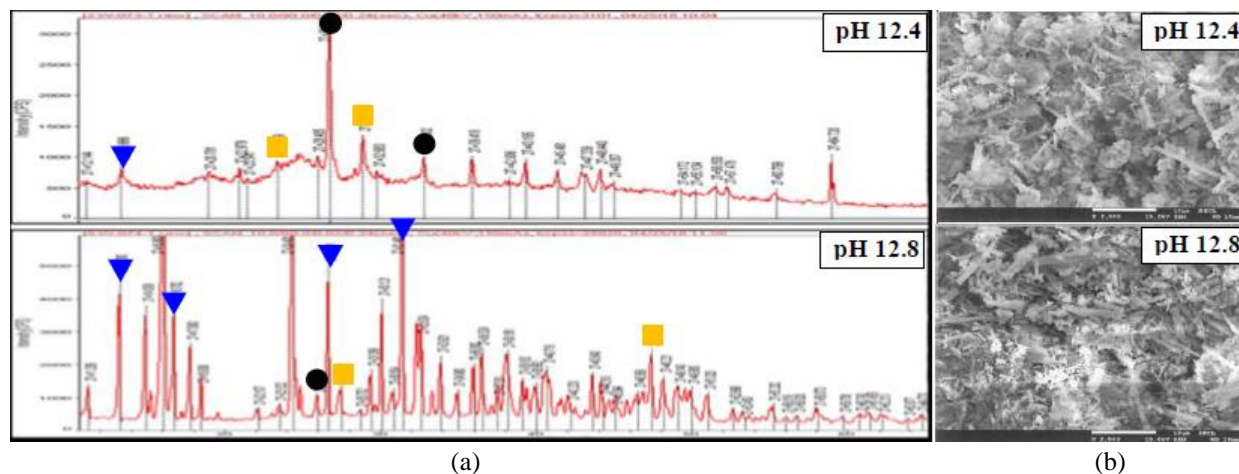


Fig. 5 XRD patterns and SEM images of precipitates harvested at different operating conditions (a) pH 12.4 and (b) pH 12.8 (▼ ettringite, ●  $\text{CaCO}_3$ , ■  $\text{CaSO}_4$ )

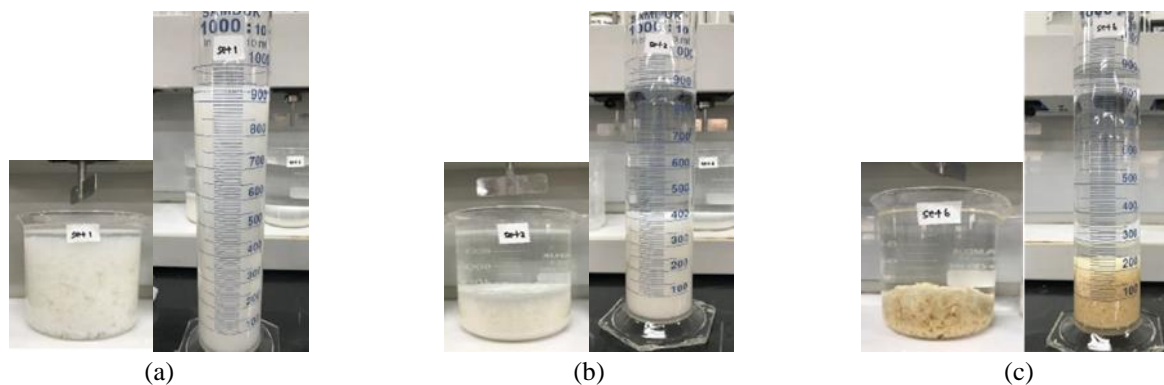


Fig. 6 The effects of aluminiferous reagents on generated sludge volume for (a)  $\text{NaAlO}_2$ , (b)  $\text{AlCl}_3$ , and (c)  $\text{AlCl}_3+\text{Fe}$

though the phase diagram in Fig. 4 would depend on the detailed aqueous compositions

The XRD, EDS and SEM analyses on the precipitated sludge after thermal treatment (for dehydration) determined morphology, elemental composition and crystalline structure, respectively (Fig. 5). In particular, elemental ratios among Al, Ca and S would be indicative of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) formation. The solids formed at pH 12.8 showed relative proportions of Al : Ca : S = 1 : 4.5 : 1.8, conforming to the composition of ettringite. The SEM images indicated an elongated prismatic shape of the precipitates, a characteristic morphology of ettringite as the main ingredient in this condition. The slightly larger fraction of Ca was believed to come from unreacted lime adsorbed to the precipitates. In comparison, at pH 12.4, the EDS results deviated from the ideal ettringite formula. The XRD (Fig. 5(a)) revealed the co-precipitated crystalline impurities such as  $\text{CaCO}_3$  and  $\text{CaSO}_4$ , suggesting that the presumed  $\text{Al}(\text{OH})_3$  impurities would be amorphous.

### 3.3 Effect of Al source reagents on $\text{SO}_4^{2-}$ removal and sludge volumes

Hinted by the detrimental effects of  $\text{Al}^{3+}$  over-dose, further batch experiments were conducted to investigate the effect of the Al source chemicals ( $\text{NaAlO}_2$ ,  $\text{AlCl}_3$ ,  $\text{AlCl}_3 + \text{Fe}$ ) on the physicochemical properties of the ettringite

sludge. In particular, the propensity to form a high-density precipitate was evaluated in terms of sludge volume.

At the given molar dose of Al, the effluent  $\text{SO}_4^{2-}$  concentration was reduced to less than 40 mg/L, regardless of the chemicals. However, as shown in Figure 6, the volumetric sludge generation was considerably dependent on Al sources. The generated sludge volume (%), after 70 min precipitation and 30 min settling, was in following orders:  $\text{AlCl}_3 + \text{Fe}$  (20%) <  $\text{AlCl}_3$  (40%) <<  $\text{NaAlO}_2$  (95%). It was interesting enough to note that  $\text{AlCl}_3 + \text{Fe}$  dramatically reduced the sludge production (~ 21% compared to  $\text{NaAlO}_2$ ) which was expected to improve the sludge dewaterability as well.

This observation agreed with the previous findings (Sapsford *et al.* 2017) that the aluminiferous reagents influenced the resultant sludge volume and sludge settling velocity. The sodium aluminate was reported to form relatively voluminous sludge with low settling velocity, presumably due to an intercalation of  $\text{Na}^+$  into the ettringite precipitates. In comparison, added Fe salt was expected to accelerate the charge neutralization and subsequent precipitation of the ettringite. The SEM images on precipitates (Fig. 7) further examined that the aluminiferous reagents clearly resulted in differentiated morphology with more compact middle round crystallites. Sludge production and dewaterability should be one of the important techno-economical indices for chemical precipitation processes,

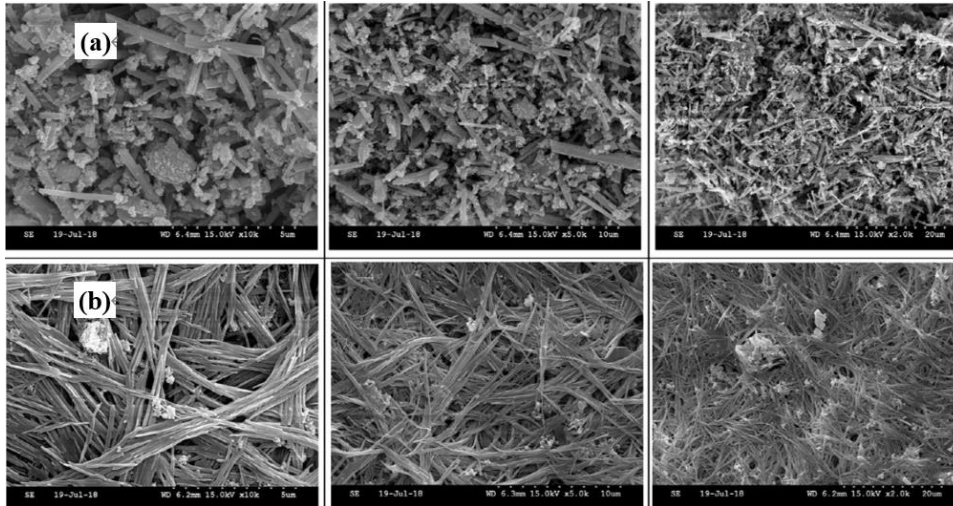


Fig. 7 Microscopic images of precipitates formed from  $\text{AlCl}_3 + \text{Fe}$  (a) and  $\text{NaAlO}_2$  (b) as indicated, highlighting differences in morphology

Table 2 Lab-scale continuous experiment results at different operation condition

Volume: 4L	pH	Sludge recycle (%)	Dosage amount		Water quality of effluent (mg/L)						
			Stoichiometric quantities of $\text{Al}^{3+}$	Stoichiometric quantities of $\text{Ca}^{2+}$	$\text{SO}_4^{2-}$	$\text{F}^-$	$\text{PO}_4^{3-}$	SS	$\text{Al}^{3+}$	$\text{Ca}^{2+}$	Si
Influent	3.35	-	-	-	1,722	479	147	-	0.4	11.7	19.1
Effluent	11.5	0	1.0	1.5	33.1	12.7	<1	9,547	31.6	815	2.18
Effluent	11.5	15	1.0	1.4	35.8	17.1	<1	9,730	17.8	706	1.21

especially when the sludge is tagged as hazardous one depending on the wastewater characteristics. Consequently,  $\text{AlCl}_3 + \text{Fe}$  reagent was selected for the subsequent continuous ettringite process. Nevertheless, the effects of chloride counterions in the effluents need to be tackled in future study, to fully confirm the applicability of  $\text{AlCl}_3$ .

### 3.4 Performance of lab-scale ettringite system

According to the batch experiments, a designed lab-scale ettringite precipitation process was operated under a continuous flow mode and the overall performance was evaluated in terms of the effluent quality with or without a sludge recycle. The continuous experiments were conducted under the operating conditions of hydraulic retention time (HRT) of 100 min, pH above 12.7, together with 1.5 and 1 of stoichiometric quantities for  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , as derived from the batch experiments. In the continuous experiments, lime was firstly added to reactor #1 for simultaneous input of  $\text{Ca}^{2+}$  and pH control. As shown in Table 2, ettringite precipitation without sludge recycle showed more than 98.1% of  $\text{SO}_4^{2-}$  removal with effluent  $\text{SO}_4^{2-}$  concentration of 33.1 mg/L, on average, for 10 days operation. In addition, the removal efficiency and effluent concentration of fluoride ion were averaged to 97.4% and 12.7 mg/L (feed fluoride concentration: 479 mg/L), owing to the concurrent  $\text{CaF}_2$  precipitate formation. The sequential addition of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  in the continuous experiments marked  $\text{SO}_4^{2-}$  removal efficiency comparable with the batch experiments

(with simultaneous addition of coagulants), since the HRT was sufficient to reach equilibrium.

When the sludge at the bottom of clarifier was recycled back to the reactor tank #1, more densification of the sludge was observed with solids concentrations up to 15%. Accordingly, a slightly decreased  $\text{Ca}(\text{OH})_2$  dosage (1.5 to 1.4 of stoichiometric  $\text{Ca}^{2+}$  dose) could give similar water treatment efficacy to benefit the process economics. There are several possible interpretations for this observation. First, the recycled sludge serves as seed and improved precipitation kinetics compared to the homogenous single pass system. In comparison, Recycling of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  leads to a decrease in  $\text{SO}_4^{2-}$  concentration because Second, the recycled ettringite sludge could liberate  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  by the acidity of influent wastewater. Finally, the influent pH could be raised due to the returned ettringite sludge (pH 12.7), since the decomposition of ettringite should produces  $\text{OH}^-$ , to rationalize the reduced lime consumptions. It should be noted that, however, there was a significant feed dilution due to recycling of the voluminous sludge entrained with water, to give an optimal sludge recycle ratio.

Consequently, the lab-scale continuous experiment confirmed that it would be possible to use the ettringite process to achieve the goal of treating  $\text{SO}_4^{2-}$  down to 250 mg/L, with reduced chemical doses by an operation engineering. The ettringite precipitation based technology can potentially be utilized to retrofit the existing semi-conductor wastewater treatment processes for  $\text{F}^-$  removal, with relatively low installation costs.

#### 4. Conclusions

In this report, an ettringite precipitation process was interrogated to meet stringent wastewater for sulfate (target effluent concentration of 250 ppm), for potential application in sulfate-rich semiconductor wastewater treatment. The treatment performance and the working mechanism were studied systemically and the key operational parameters were identified. Lab-scale batch and continuous experiments were performed at various operating conditions. The best experimental conditions observed were summarized as the sequential uses of  $\text{Ca}(\text{OH})_2$  and  $\text{AlCl}_3 + \text{Fe}$  with 1.5 of stoichiometric quantities of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  at pH above 12.7. The effluent  $\text{SO}_4^{2-}$  concentrations lower than 50 mg/L were achievable in the continuous process. The optimized process in this study would be simpler, highly feasible and cost-effective for industrial application of sulfate-rich wastewater treatment compared to other sulfate removal technologies. Further investigation is warranted as a pilot-scale investigation to guarantee a long-term performance and techno-economical benefits to retrofit the existing facilities.

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#### References

- Aygun, A., Dogan, S. and Argun, M.E. (2018), "Statistical optimization of ettringite precipitation in landfill leachate", *Brazil J. Chem. Eng.*, **35**, 969-976. <https://doi.org/10.1590/0104-6632.20180353s20170528>.
- Baird, R.B., Eaton, A.D. and Clesceri, L.S. (2012), *Standard Methods For The Examination of Water And Wastewater*, American Public Health Association, Washington, DC., U.S.A.
- Bertolino, S.M., Veloso, T.C. and Leão, V.A. (2011), "Performance of a lactate-fed UASB reactor treating sulfate containing waters", *Proceedings of the 11th International Mine Water Association Congress, Mine Water – Managing the Challenges*, Aachen, Germany, September.
- Bowell, R. (2004), "A review of sulfate removal options for mine waters", *Proceedings International Mine Water Association Symposium*, Newcastle upon Tyne, U.K., September.
- Dou, W., Zhou, Z., Jiang, L.M., Jiang, A., Huang, R., Tian, X., Zhang, W. and Chen, D. (2017), "Sulfate removal from wastewater using ettringite precipitation: magnesium ion inhibition and process optimization", *J. Environ. Manag.*, **196**, 518-526. <https://doi.org/10.1016/j.jenvman.2017.03.054>.
- Germishuizen, C., Franzsen, S., Grobler, H., Simate, G. and Sheridan, C. (2018), "Case study modelling for an ettringite treatment process", *Water SA*, **44**(1), 86-92. <https://hdl.handle.net/10520/EJC-c670364c1>.
- Guo, S., Luo, J., Wu, Y., Qi, B., Chen, X. and Wan, Y. (2018), "Decoloration of sugarcane molasses by tight ultrafiltration: filtration behavior and fouling control", *Sep. Purif. Technol.*, **204**, 66-74. <https://doi.org/10.1016/j.seppur.2018.04.067>.
- Hampsoim, C. and Bailey, J. (1982), "On the structure of some precipitated calcium aluminosulphate hydrates", *J. Mater. Sci.*, **17**(11), 3341-3346. <https://doi.org/10.1007/BF01203504>.
- Kabdaşlı, I., Bilgin, A. and Tünay, O. (2016), "Sulphate control by ettringite precipitation in textile industry wastewaters", *Environ. Technol.*, **37**(4), 446-451. <https://doi.org/10.1080/09593330.2015.1026245>.
- Moore, A. and Taylor, H.F.W. (1968), "Crystal structure of ettringite", *Nature*, **218**, 1048-1049. <https://doi.org/10.1038/2181048a0>.
- Nguyen, H.T., Cho, K., Jang, A. and Jeong, S. (2021), "Cost analysis and scheduling of the desalination vessel using reverse osmosis technology", *Membr. Water Treat.*, **12**(4), 177-185. <https://doi.org/10.12989/mwt.2021.12.4.177>.
- Norapat, P., Siwat, S., Yothin, C. and Pimluck, K. (2021), "Sulfate removal from lignite coal mine drainage in Thailand using ettringite precipitation", *Chemosphere*, **285**, 131-357. <https://doi.org/10.1016/j.chemosphere.2021.131357>.
- Pikaar, I., Sharma, K.R., Hu, S., Gernjak, W., Keller, J. and Yuan, Z. (2014), "Reducing sewer corrosion through integrated urban water management", *Science*, **345**(6198), 812-814. <https://doi.org/10.1126/science.1251418>.
- Sapsford, D.J. and Tufvesson, S. (2017), "Properties of recycled sludge formed from different aluminiferous reagents during the ettringite process", *J. Water Proc. Eng.*, **19**, 305-311. <https://doi.org/10.1016/j.jwpe.2017.08.016>.
- Silva, R., Cadorn, L. and Rubio, J. (2010), "Sulphate ions removal from an aqueous solution: I. Co-precipitation with hydrolysed aluminum-bearing salts", *Miner. Eng.*, **23**(15), 1220-1226. <https://doi.org/10.1016/j.mineng.2010.08.016>.
- Tait, S., Clarke, W.P., Keller, J. and Batstone, D.J. (2009), "Removal of sulfate from high-strength wastewater by crystallisation", *Water Res.*, **43**(3), 762-772. <https://doi.org/10.1016/j.watres.2008.11.008>.
- Tolonen, E.T., Hu, T., Rämö, J. and Lassi, U. (2016), "The removal of sulphate from mine water by precipitation as ettringite and the utilisation of the precipitate as a sorbent for arsenate removal", *J. Environ. Manag.*, **181**, 856-862. <https://doi.org/10.1016/j.jenvman.2016.06.053>.
- Usinowicz, P.J., Monzyk, B.F. and Carlton, L. (2006), "Technical and economic evaluation and selection of sulfate ion removal technologies for recovery of water from mineral concentrate transport slurry", *Proceedings of the Water Environment Federation*, **13**, 139-153. <https://doi.org/10.2175/193864706783710695>.

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