Properties of recycled sludge formed from different aluminiferous reagents during the ettringite process

D.J. Sapsford*, S. Tufvesson

Cardiff School of Engineering, Cardiff University, UK

ARTICLE INFO

ABSTRACT

Development of processes for the removal of sulfate ions from mine waters and industrial effluents is ongoing. A number of processes involve the removal of sulfate as ettringite, a calcium aluminum sulfate $(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O)$ at elevated pH (11.5–13). Various process configurations have been proposed using lime in combination with an aluminiferous reagent to react with the sulfate in the effluent. This paper presents a study of the effect of the source of aluminum (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 recycled, to form high density sludge (HDS). It is demonstrated that aluminum chloride, aluminum nitrate and polyaluminum chloride all remove sulfate as ettringite, with aluminum chloride removing sulfate to the lowest residual concentration. Sodium aluminate proved least effective at removal of sulfate for > 1 cycle, and early process cycles produced a precipitate that may have been a mixture of minerals including ettringite and calcium aluminate monosulfate. Laboratory synthesised aluminum hydroxide and crystalline gibbsite were unreactive to sulfate. The different aluminiferous reagents influenced the resultant sludge volume and sludge settling velocity, with sodium aluminate forming a relatively voluminous sludge with low settling velocity and aluminum chloride-derived ettringite forming the densest 'single-pass' sludge and consistently the fastest settling sludge. Recycling of sludge in the process seemingly improves the precipitation kinetics, with lower residual sulfate concentrations found for the same reaction time upon sludge recycling. All sludges showed a slight propensity to form HDS upon recirculation. Microscope images show differences in the precipitate morphology between different aluminiferous reagents and upon recycling of sludge, typically there was an evolution from small spherical precipitates to increasing amounts of needle-shaped crystals upon recycling. These results highlight the importance of understanding how the choice of aluminiferous reagent influences the micro- and macroscopic properties of the resultant sludge, with the commensurate implications this has for process design when applying the ettringite precipitation process for the removal of sulfate from effluents.

1. Introduction

Elevated concentrations of the sulfate ion ($SO_4^{2-}_{(aq)}$) occur in a range of mining and industrial effluents including mine drainage; mineral slurry transport water; effluents from smelting operations; hydraulic fracturing flow back; effluents from the manufacture of paper, textiles, fertilisers, dyes, glass, soaps, fungicides, and tanneries [1,2]; and root crop processing e.g. ginger and beet and aluminum anodising [3].

Sulfate is not regarded as toxic to humans at the levels typically encountered in the environment. However, sulfate is regarded as an aesthetic pollutant in drinking water with the taste threshold generally lying between 250 mg/L and 1000 mg/L for sodium and calcium sulfate respectively. The World Health Organisation (WHO) recommends a 250 mg/L threshold [4]. Waters and effluents containing in excess of 500 mg/L sulfate are considered potentially hazardous to concrete [5] affecting infrastructure such as sewers through damage caused by the formation of secondary ettringite. In recent years environmental regulators have become more concerned with high sulfate concentrations in effluents and different countries have adopted a range of approaches to regulating sulfate with many setting specific sulfate limits. Sulfate is also indirectly a target of regulation through tightening of Total Dissolved Solids (TDS) limits in many juristictions where sulfate comprises a key contributor to the elevated TDS [6].

Removal technologies for sulfate from sulfate-rich effluents have been reviewed (e.g. [7,6] and include (i) chemical addition to induce the precipitation of insoluble/sparingly-soluble sulfate salts including

gypsum, ettringite (e.g. [8]; barium sulfate (e.g. [9,10] and jarosite (e.g. [11]; (ii) removal using membrane processes such as electrodialysis, reverse osmosis and nanofiltration (iii) ion exchange (iv) biological treatment − utilising microbiological sulfate reducing organisms, and (v) evaporation/crystallisation. It is noteworthy that membrane processes comprise only partial treatment in that a reject sulfate brine is produced which will require chemical precipitation or evaporative crystallisation to produce a solid for final disposal. With respect to the chemical precipitation processes, ettringite precipitation processes are considered particularly promising [6]. The reaction occurs at elevated pH (11.5–13) and involves reaction of dissolved sulfate with aluminum and calcium reagents such that ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) precipitates. This paper concerns the composition, morphology, and mineralogy of precipitates that form during the ettringite process for the removal of sulfate.

The term ettringite is used to refer to both the mineral and the ettringite crystal structure [12,13]. Parallel columns comprising Ca^{2+}, Al^{3+} and $OH^−$ structured units of $[Ca_6Al_2(OH)_{12}.24H_2O]^{6+}$ are characteristic of the ettringite crystal structure. Water and sulfate ions exist within channels formed between the structural columns which balance out the structural charge [14,13]. The mineral can exchange some of its ions without adverse structural change [13] and the water content can be variable with between 24 and 32 moles of water per mole of ettringite but this does not impact the XRD response upon analyses [12]. Most literature regarding ettringite comes from the field of concrete technology and waste stabilisation (e.g. [15] as ettringite is a common constituent phase important in developing early stage strength and also causes problematic secondary or delayed ettringite formation. Consequently, literature on physicochemical and morphological aspects of ettringite relevant to this study focuses on much slower processes in concrete rather than the short residence times within water treatment processes. Nevertheless, there are several useful insights − Cody et al. [16] investigated how the nucleation and growth of the ettringite crystals were affected by different chemicals and demonstrated that different precipitate morphologies result from the presence of a range of additives and their concentration.

With respect to the literature on ettringite during sulfate removal processes for effluent treatment, there are only a small number of publications covering the effectiveness of different reagents in removing sulfate as ettringite (e.g. Janneck et al. [17] and there is an absence of studies looking at the influence of aluminiferous reagent and sludge recycling on the physicochemical properties of the resultant sludge. This study came about after preliminary trials of an ettringite precipitation process indicated problematic volumes of precipitate. Similar problems with voluminous 'single-pass' sludge has commonly experienced with metal precipitation from mine waters and industrial effluents with typical sludges having a solids contents of only 1–5%. The High Density Sludge (HDS) process was developed in response to this problem [18,19]. Process sludge is recycled from the clarifier to the reactor tanks leading to densification of the sludge to solids concentrations of 15–35%, improved settling velocities, dewaterability and reduced resistance to filtration which equates to better process economics [20]. It was noted that some of the current proprietary ettringite precipitation processes involve sludge recycling. Thus the aims of this study were to (i) ascertain the properties of single pass sludge for different aluminiferous reagents, and (ii) to determine how residual sulfate, settling rates, sludge volume, morphology, chemical composition and mineralogy vary when recycling sludge using different aluminiferous reagents.

2. Materials and methods

The experiments were carried out as bench scale batch tests and adapted from the HDS experiments of Bosman [21]. The experiments involved treatment of a sodium sulfate feed by addition of stoichiometric quantities of aluminiferous reagent and a 10% stoichiometric

excess of lime. The feed was limited to $[SO_4^{2−}] = 1500$ mg/L to avoid precipitation of gypsum. The reagents were used in solution or slurry-form prepared in deionized water and of the following strengths (% w/v): sodium sulfate (Na_2SO_4) − 2.22% solution; calcium hydroxide ($Ca(OH)_2$) − 5% slurry (kept suspended using a magnetic stirrer). Aluminiferous reagents used were as follows: aluminum chloride ($AlCl_3 \cdot 6H_2O$) − 25% solution; sodium aluminate − 8.5% $NaAlO_2$ solution; polyaluminum chloride (PAC) − 10% solution; aluminum nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) − 22%; aluminum hydroxide ($Al(OH)_3$) powder; and synthesised aluminum hydroxide. The synthesised aluminum hydroxide was produced by neutralising 250 ml of a 2% $AlCl_3$ solution with NaOH. This resulted in a gel which was filtered, rinsed thoroughly with deionized water and dried at 105 °C for 48 h.

The batch tests were conducted either as 'single pass' or as 'recycled' as follows: 100 ml (± 1 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 addition of aluminiferous reagent. Immediately afterwards an additional 1.1 ml $Ca(OH)_2$ was added. The suspension was stirred for 15 min and pH recorded. The suspension was transferred to a volumetric measuring cylinder and the sludge allowed to settle for 15 min. A 15 min settling period (rather than 30 min typically used in similar studies) was found to achieve acceptable liquid/solid separation and was used throughout the experimentation, this made experiments with multiple repeat cycles more practicable. During the 15 min the volume of settled sludge and the distance the sludge had settled were continuously recorded to allow the settling velocity to be calculated. 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 6 cycles for $NaAlO_2$, PAC and $Al(NO_3)_3 \cdot 9H_2O$. Because of the promising performance of $AlCl_3$, this reagent was used for 12 cycles. The aluminum hydroxide powder was only taken through 1–3 cycles and thereafter discontinued.

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 for 24 h 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 h) and weighed. The dry samples were analyzed by X-Ray Diffraction (XRD) performed using a Phillips Philips PW1710 Xpert Pro diffractometer with a CoKa radiation source (generator voltage of 40 keV; tube current of 30 mA). Spectra were acquired between 2 h angles of 5–90°, with a step size of 0.02° and a 2 s dwell time. Following the XRD analysis the dried samples were acid digested and analyzed using the Perkin Elmer Optima 2100 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for Ca, S and Al.

3. Results and discussion

3.1. Effectiveness of aluminum hydroxide as an aluminiferous reagent

For the single pass experiments significant sulfate removal was only observed with $AlCl_3$, $NaAlO_2$, PAC and $Al(NO_3)_3$. The XRD and ICP-OES results for both the powdered and the laboratory synthesised aluminum hydroxide showed virtually no sulfate removal and no sign of ettringite being formed. Attempts of recycling did not change these results and it was deemed that aluminum hydroxide in these forms was not able to react to produce ettringite. This is in agreement with the findings of Janneck et al. [17] who found that none of the three crystalline $Al(OH)_3$-based reagents were able to substantially reduce sulfate concentrations, attributed to the reagent not being "active". Despite this,