Use of 24 kHz ultrasound to improve sulfate precipitation from wastewater

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A B S T R A C T

Elevated sulfate concentrations in industrial effluent can lead to a number of significant problems, the most serious of which is the corrosion of concrete sewers as a result of hydrogen sulfide induced biogenic sulfuric acid attack; hydrogen sulfide can also create odor nuisance problems. The most common treatment process for sulfate removal from wastewaters is to precipitate it as gypsum using lime addition. Nevertheless, meeting discharge consent limits for sulfate can often present practical challenges due to the solubility of gypsum and so there is a need to investigate technological solutions that might provide for more consistent sulfate removal.

This paper reports on the application of ultrasound during the sulfate precipitation process. We show that with as little as 10 s sonication at 24 kHz, significant increases in the rate of sulfate precipitation are observed. Particle size analysis, pH profiles and SEM micrographs, suggest that the likely mode of action is disaggregation of the calcium hydroxide particles, giving a greater solid–liquid interface, thus resulting in a faster dissolution rate and more readily available calcium ions. A range of experimental variables are studied, including the duration and power of sonication, as well as initial sulfate concentration and the effect of changing the time at which sonication is applied. For both sonicated and non-sonicated samples, precipitation commences almost immediately that the lime is added and so induction time is not an issue in this system.

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1. Introduction

High levels of sulfate in industrial effluent can give rise to numerous problems in sewage systems including corrosion of metal and concrete as a result of biogenic sulfuric acid attack [1–3]. In this process, anaerobic bacteria in the sewage system reduce sulfate to hydrogen sulfide which partitions into the gaseous phase where, along with oxygen, it can diffuse into the moist biofilms present on the sewer walls. Subsequently, the hydrogen sulfide is oxidized to sulfuric acid in the biofilms by bacteria such as Acidithiobacillus thiooxidans [3]. An additional problem is that hydrogen sulfide is toxic at high concentrations (8 h time weighted average exposure limit of 7500 μg m m−3 [4]) and is an odor nuisance even at very low concentrations (odor detection threshold of 0.705 μg m−3 [5]). For these reasons, regulators will often specify a discharge consent limit for sulfate in wastewater. Precipitation with calcium hydroxide, as lime or lime slurry, is the most economic treatment method, but consent limits may be very close to the published solubility of calcium sulfate (1467 mg L−1 as sulfate at 25 °C [6]). Therefore, achieving these consent limits may present practical difficulties and so there is a need to investigate methods that will result in more effective and consistent sulfate removal.

With this context we report on the application of 24 kHz ultrasound to improve the precipitation of calcium sulfate from a simulated acidic sulfate effluent. There have been several studies that have investigated the effect of ultrasound on precipitation of various salts from super-saturated solutions, for example calcium sulfate [7], barium sulfate [8] and calcium carbonate [9], where ultrasound is found to reduce the induction time for precipitation or crystallization [7,9,10]. However, there have been few studies that have looked at reactions where the precipitant is a sparingly soluble solid and, to our knowledge, none that have used calcium hydroxide. In this latter case, in addition to the potential for ultrasound-induced nucleation [9], the effect of ultrasonic radiation on the calcium hydroxide suspension will also be important.

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The motivation for this research arose from a pilot-scale project looking at ultrasonic enhancement of the precipitation of acidic sulfate-containing wastewater from a large UK manufacturing facility and the need to fully understand the factors involved. The pilot plant has recently been upgraded to a full scale treatment process.

2. Experimental section

2.1. Model simulation of sulfate precipitation from acidic sulfate effluent

It was useful to first carry out some model simulations of the sulfate precipitation reaction in the absence of ultrasound in order to get an overview of the expected concentrations of the key species involved. We used OLI’s Stream Analyzer software (Cedar Knolls, NJ, USA) [11], to simulate the equilibrium concentrations of sulfate, bisulfate, and calcium for a 7340 mg L\(^{-1}\) sulfuric acid solution (7200 mg L\(^{-1}\) sulfate) when titrated with solid calcium hydroxide at 25 °C under the conditions used in the subsequent experimental study described in Section 2.2 (including the addition of 0.766 g L\(^{-1}\) HCl and 0.60 g L\(^{-1}\) aluminum chloride). The thermodynamic framework of the model, which is widely used in the wastewater treatment industry, is detailed in the literature [12]. The model considered the equilibria of three solid phase species (Ca(OH)\(_2\), CaSO\(_4\)\(2\)H\(_2\)O and Al(OH)\(_3\)), together with 19 aqueous phase species (HCl, Al(OH)\(_2\)Cl, SO\(_4\), CaSO\(_4\), CaCl\(_2\), H\(^+\), Ca\(^{2+}\), CaOH\(^+\), OH\(^-\), HSO\(_4\), SO\(_4\), Ca\(^{2+}\), Cl\(^-\), Al(SO\(_4\))\(_2\), Al(OH)\(_3\), Al(OH)\(_4\), AlSO\(_4\), AI\(_{0.5}\)OH\(_{1.5}\) and AI\(_{0.5}\)OH\(_{1.5}\)).

2.2. Experimental study

2.2.1.Overview

The aim of the experimental study was to characterize the effect of ultrasound on the precipitation of SO\(_4\)\(^{2-}\) from simulated acidic sulfate effluent (H\(_2\)SO\(_4\)) subsequent to the addition of calcium hydroxide. The concentration of SO\(_4\)\(^{2-}\), solution pH and particle size distribution were all measured as a function of time. In addition, dried samples of the precipitate were observed using scanning electron microscopy (SEM) fitted with an energy dispersive spectrometer (EDS), allowing the morphology and elemental composition of the components of the precipitate to be investigated. In addition to sulfate removal efficiency, sedimentation characteristics of the precipitate are important when considering the industrial application of this process; this was investigated in a further series of precipitation experiments in which sedimentation volume was determined as a function of time.

2.2.2. Reagents

Hydrochloric acid (32%) and sulfuric acid (95%) both of analytical reagent grade were supplied by Fisher Scientific (Loughborough, UK). Pluspac 1000, a 10% solution of polyaluminium chloride, was supplied by Feralco (Widnes, UK). Calcium hydroxide was supplied by Sigma Aldrich (Poole, UK). For the sedimentation experiments, a heavy metal precipitant, EPOLOC L1-R (5%) was used, together with an anionic polyacrylamide (0.2%) flocculent (Cleanfloc AES3H), both supplied by Aqua-Technik (Neuenkirchen, Germany). Barium chloride tablets used for the SO\(_4\)\(^{2-}\) determination were supplied by Palintest Ltd. (Gateshead, UK).

2.2.3. Experimental set-up for the precipitation experiments

Precipitation experiments were carried out using 500 mL samples of acidic sulfate effluent contained in a 500 mL glass beaker. The beaker was located in a water bath at 25 °C and the sample was stirred using a submersible magnetic stirrer.

For sonication experiments, ultrasound was applied using a 24 kHz Hielscher UP400S model sonicator (Tetlow, Germany) fitted with an H22 horn (cylindrical, 22 mm tip diameter). The maximum acoustic power density at the sonotrode surface for the H22 horn is 85 W cm\(^{-2}\), adjustable to between 0% and 100% using the power control setting. A Volctraft Energy Check 3000 meter was used to monitor the power consumption of the sonotrode. The sonotrode was placed in the sample at the recommended submerge depth of 45 mm.

2.2.4. Precipitation procedure

Precipitation experiments, either with or without sonication, were carried out using the experimental configuration described in Section 2.2.3. Appropriate concentrations of simulated acidic sulfate effluent (between 4000 and 15,200 mg L\(^{-1}\) SO\(_4\)\(^{2-}\)) were obtained by dilution from a 4 M stock solution of H\(_2\)SO\(_4\). The following procedure was used for the experiments: (a) further acidification of the 500 mL sample of acidic sulfate effluent using 0.766 g L\(^{-1}\) concentrated HCl; (b) addition of 0.6 g L\(^{-1}\) polyaluminium chloride (Pluspac 1000); and (c) addition of calcium hydroxide in powder form. For those experiments where sonication was carried out, the sonicator was switched on for between 5 and 20 s immediately upon addition of the calcium hydroxide. The sonotrode power output was set at between 35% and 45% of the maximum, depending on the required experimental conditions. The ranges of experimental parameters used in these studies, including reagent volumes, sonication duration and acoustic power density, were initially optimized for maximum SO\(_4\)\(^{2-}\) removal during a series of preliminary experiments in which the soluble sulfate concentration was measured at 40 min subsequent to calcium hydroxide addition.

2.2.5. Sulfate determination

The concentration of SO\(_4\)\(^{2-}\) was monitored over the course of the reaction using a turbidimetric method. Samples of the reaction solution were taken at 1 min intervals for the first 12 min and increasing intervals thereafter. Prior to SO\(_4\)\(^{2-}\) analysis, the sample was passed through a 0.2 μm syringe filter (Phenomenex, Macclesfield, UK) to remove the precipitate. The filtrate was then diluted with distilled water so as to be within the range of the turbidimetric method used to measure the SO\(_4\)\(^{2-}\). Depending on the stage of the reaction this dilution would be between 10- and 40-fold. The turbidimetric method requires the dissolution of a tablet containing 20 mg barium chloride in 10 mL of sample, leaving to stand for 5 min whilst the barium sulfate precipitate fully develops, then measuring the turbidity, which is proportional to the SO\(_4\)\(^{2-}\) concentration. The measurements were carried out using a Palintest 7100 photometer. The method has a range of 0–200 ± 2 mg L\(^{-1}\) SO\(_4\)\(^{2-}\). The output of the instrument is directly in mg L\(^{-1}\) SO\(_4\)\(^{2-}\), though calibrations on known concentrations of sulfuric acid were performed to verify the accuracy of the procedure for this particular application. In addition, pH was monitored at the same time intervals as for the SO\(_4\)\(^{2-}\) determination.

2.2.6. Sedimentation characteristics

Sedimentation characteristics of the precipitate were investigated in a further series of precipitation experiments in which sedimentation was aided by the addition of a synthetic flocculent so as to simulate practical removal processes. The same precipitation procedure outlined above was followed with the exception that 0.1 mL of heavy metal precipitant (Epofloc L1-R) and 0.1 mL of anionic polyacrylamide flocculent were added to the solution 30 s after addition of the calcium hydroxide. The solution was then stirred for 10 min before allowing to settle in a 500 mL beaker. The volume of the sediment in mL (±5 mL) was recorded as a function of time.
2.2.7. Precipitate analysis

Characteristics of the precipitate were determined from EDS, SEM and particle size analysis. Changes in particle size distribution during the course of the reaction, both in the presence and absence of ultrasound, were determined using a Malvern Instruments Mastersizer 2000 instrument (Malvern, UK). This same analysis was also carried out for a sample in which calcium hydroxide was added to distilled water alone so as to observe its disaggregation properties. Information about the composition of the precipitate was obtained from SEM analysis using an FEI Quanta 200 instrument fitted with an Oxford Instruments EDS (Abingdon, UK). For the EDS and SEM analysis, samples of precipitate, either from non-sonicated or sonicated samples, were prepared by pipetting onto a glass microscope slide to form a thin film before drying at 40 °C for 24 h. EDS was performed on uncoated samples; these were subsequently coated with gold to obtain the SEM micrographs.

3. Results

3.1. Model simulation results

Upon the addition of lime to sulfate-containing effluent, the SO$_4^{2-}$ precipitates out as gypsum (CaSO$_4\cdot$2H$_2$O) according to Eq. (1); this is the most stable form of calcium sulfate under the conditions used in this study [13].

$$SO_4^{2-}(aq) + Ca^{2+}(aq) + 2H_2O \rightleftharpoons CaSO_4 \cdot 2H_2O(s) \tag{1}$$

Fig. 1 shows the results of a model simulation using OLI’s Stream Analyzer software [11]. The model simulated the equilibrium concentrations of sulfate, bisulfate, and calcium, for a 7340 mg L$^{-1}$ sulfuric acid solution (7200 mg L$^{-1}$ SO$_4^{2-}$) when titrated with solid calcium hydroxide at 25 °C under the conditions used in the experimental part of this study. At 25 °C the minimum concentration of SO$_4^{2-}$ predicted to remain in solution is 937 mg L$^{-1}$ (reached at 8.5 g L$^{-1}$). This is similar to the observed equilibrium concentrations listed in Table 1 for precipitation experiments carried out with the corresponding sulfuric acid concentration under various conditions, as described later in this section. The simulation also predicts that the solid phase will comprise 2.8 g L$^{-1}$ unreacted CaOH$_2$ (20% of solids) and 11.9 g L$^{-1}$ gypsum (80%) and that the solution pH will be 12.3, which was also observed in practice. The equilibrium concentration of SO$_4^{2-}$ is highly dependent upon temperature as shown in a further simulation shown in Fig. 2. Partridge and White found that above 98 °C the anhydrite and hemihydrates are the solid phases most likely to form [14].

![Fig. 1. Predicted solution pH and equilibrium concentrations at 25 °C for sulfate, bisulfate and calcium ions for 7.35 g L$^{-1}$ solution of sulfuric acid that is titrated with various amounts of calcium hydroxide (added in 0.2 g steps). Modelling was carried out using Stream Analyzer published by OLI Systems [11,12].](image)

Table 1

<table>
<thead>
<tr>
<th>Initial [SO$_4^{2-}$]/mg L$^{-1}$</th>
<th>Sonication duration/s</th>
<th>Power/ W cm$^{-2}$</th>
<th>Rate/min$^{-1}$</th>
<th>Measured [SO$_4^{2-}$]/mg L$^{-1}$ at 57 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>7200</td>
<td>0</td>
<td>n/a</td>
<td>0.153 ± 0.009</td>
<td>920</td>
</tr>
<tr>
<td>7200</td>
<td>5</td>
<td>32.9</td>
<td>0.255 ± 0.011</td>
<td>1080</td>
</tr>
<tr>
<td>7200</td>
<td>10</td>
<td>33.5</td>
<td>0.294 ± 0.021</td>
<td>840</td>
</tr>
<tr>
<td>7200</td>
<td>20</td>
<td>33.6</td>
<td>0.220 ± 0.015</td>
<td>1000</td>
</tr>
<tr>
<td>7200</td>
<td>20</td>
<td>38.3</td>
<td>0.309 ± 0.016</td>
<td>1000</td>
</tr>
<tr>
<td>4000</td>
<td>0</td>
<td>33.7</td>
<td>n.d.</td>
<td>1960</td>
</tr>
<tr>
<td>4000</td>
<td>10</td>
<td>33.7</td>
<td>n.d.</td>
<td>1980</td>
</tr>
<tr>
<td>15,500</td>
<td>0</td>
<td>34.1</td>
<td>0.301 ± 0.073</td>
<td>700</td>
</tr>
<tr>
<td>15,500</td>
<td>10</td>
<td>34.1</td>
<td>0.836 ± 0.059</td>
<td>700</td>
</tr>
</tbody>
</table>

The error for this technique is ±10 mg L$^{-1}$.

![Fig. 2. Predicted equilibrium sulfate concentrations over the temperature range 5 to 96 °C for a mixture of 11.75 g L$^{-1}$ Ca(OH)$_2$ and 7.35 g L$^{-1}$ H$_2$SO$_4$ at 25 °C. Modelling was carried out using Stream Analyser published by OLI Systems [11,12].](image)

3.2. Effect of sonication on precipitation rates

Optimal ranges of sonication parameters and reagent volumes were determined from an initial series of experimental runs that measured the SO$_4^{2-}$ concentration remaining in solution at 40 min subsequent to calcium hydroxide addition. Addition of polyaluminum chloride was found to be the most important factor determining the final SO$_4^{2-}$ concentration, consistent with literature observations of the effectiveness of use of aluminum reagents in these systems [15]. Nevertheless the amount of polyaluminum chloride used in these experiments (0.6 g L$^{-1}$) reflects the economic considerations of its use in practical applications. Further acidification of the acidic sulfate effluent by HCl prior to lime addition was also found to be important. For the sonication parameters, duration of sonication did not have a significant effect on the concentration of SO$_4^{2-}$ remaining in solution, though the acoustic power density was significant, with an optimal range of between 35% and 45% of the maximum (85 W cm$^{-2}$). These ranges were used in subsequent experiments.

Whilst the equilibrium concentration of SO$_4^{2-}$ is clearly a significant factor, the rate at which the precipitation occurs is also of importance, particularly in the context of reactor design. Previous studies have shown that there is usually an induction period prior to precipitation, with the length of this period depending primarily on the degree of supersaturation [13]. At an initial SO$_4^{2-}$ concentration of 7200 mg L$^{-1}$, we observed a barely detectable induction period for both sonicated and non-sonicated samples, as shown...
in Fig. 3. Here, both $SO_4^{2-}$ concentration and pH were monitored subsequent to calcium hydroxide addition. After a short lag phase, reduction in $SO_4^{2-}$ concentration approximates to a single exponential decay for both the sonicated and non-sonicated samples, allowing the determination of pseudo-first order precipitation rates. It is clear that the rate of $SO_4^{2-}$ removal is significantly accelerated by a 10 s sonication period, with respective rates of 0.153 and 0.294 min$^{-1}$, as detailed in Table 1. In addition, the pH profile in the presence of ultrasonic irradiation, is much steeper than that without, indicating that sonication is probably acting to increase the dissolution rate of calcium hydroxide. The final concentration of $SO_4^{2-}$ remaining in solution, also detailed in Table 1, is marginally higher for the non-sonicated sample ($920 \pm 40 \text{ mg L}^{-1}$) compared to that of the sonicated ($840 \pm 40 \text{ mg L}^{-1}$). Both of these are in agreement with the concentration predicted from the modeling study (Fig. 1).

3.3. SEM and particle size analysis

Particle size (Figs. 4 and 5) and SEM analysis (Fig. 6) provides a very important insight into the processes occurring in these precipitation reactions, both in the presence and absence of sonication. Fig. 4 shows the particle size distribution in a stirred solution of calcium hydroxide alone at 3, 8 and 57 min, with and without sonication being applied at 2 min. At 3 min there is a clear difference in distribution between the two, with a distinct sub-micron fraction present for the sonicated sample, but not for the non-sonicated; the maximum of the larger peak is also shifted to a slightly lower size (from 36 $\mu$m to 32 $\mu$m) for the sonicated sample. These observations are mirrored by the SEM micrographs of calcium hydroxide alone shown in Fig. 6(a and b). Large aggregates are observed for the non-sonicated sample, Fig. 6(a), whereas significant disaggregation is evident for the sonicated sample, Fig. 6(b). At longer stirring times in Fig. 4, a sub-micron fraction does appear in the non-sonicated sample, though at 8 min it is about half the size of the corresponding peak for the sonicated sample; additionally, the shift in size distribution of the main peak for sonicated and non-sonicated appears to increase in magnitude compared to 3 min. Thus, whilst stirring alone will achieve sub-micron particle size distributions, sonication to increase in magnitude compared to 3 min. Thus, whilst stirring

Fig. 3. Reduction in sulfate concentration subsequent to calcium hydroxide powder addition in the presence (squares) and absence (circles) of sonication. Calcium hydroxide was added at 2 min. The reactant concentrations were 11.75 g L$^{-1}$ Ca(OH)$_2$ and 7.35 g L$^{-1}$ H$_2$SO$_4$. For the sonicated sample, ultrasound was applied for 10 s at a frequency of 24 kHz, and a power density of 33.5 W cm$^{-2}$ immediately upon addition of the calcium hydroxide. The curves are the best fits to a single exponential decay. The dashed and dotted lines show the pH of the non-sonicated and sonicated samples respectively.

Fig. 4. Change in particle size distribution of a stirred mixture calcium hydroxide at various times after addition of the calcium hydroxide powder to distilled water. The solid line represents the sample where no sonication was applied, whereas the dashed line represents a sample for which 10 s sonication was applied at a frequency of 24 kHz, and a power density of 33.5 W cm$^{-2}$ immediately upon addition of the calcium hydroxide.

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situation is observed for the sonicated sample, as shown in Fig. 5(b). The broad peak at 2 min, corresponding to pre-sonication is shown, but subsequent to sonication a peak with a maximum at 7 μm appears, together with a sub-micron peak. The larger peak centered on 7 μm will correspond to both fragments of the larger crystals that were present at 2 min and with calcium hydroxide. The SEM micrographs shown in Fig. 6(e) and the higher resolution image in Fig. 6(f) show the aftermath of sonication (at 3 min); here the ‘butterfly’ crystals are irregular and much reduced in size; there are also smaller planer fragments. It is likely that sonication has caused the crystals to break apart along the grain boundaries: such boundaries are evident in Fig. 6(c and f). With increased stirring times the sonicated sample shows a relatively consistent size distribution, though there was also growth of a shoulder between 10 and 100 μm, most likely due to the re-growth of larger ‘butterfly’ and ‘flower’-like calcium sulfate crystals.

Finally it should be noted that some smaller rod-like crystals were observed in the sonicated sample; the EDS analysis was consistent with these being entirringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O), formed from additional reaction in the presence of aluminum.

3.4. Sedimentation characteristics

A further important consideration in precipitation reactions is the sedimentation characteristics, particularly the rate at which this occurs and the final settled volume. Fig. 7 shows the effect of sonication on the degree of settling over a 1 h period, both with and without the addition of flocculent. It is clear that sonication increases the settling times, though the situation improves with addition of flocculent, for which the final settled volume is the same as with the non-sonicated sample. Somewhat unexpectedly, the addition of flocculent to the non-sonicated sample causes a slight increase in settling time.

3.5. Effect of sonication duration, power and timing

As described in Section 3.1, preliminary experiments were carried out in order to determine an optimal range of sonication conditions to achieve the lowest equilibrium SO₄²⁻ concentrations. Within these constraints a number of parameters relating to the application of ultrasonic irradiation were varied in order to determine the effect that these had on both the rate of precipitation and the concentration of SO₄²⁻ attained at the end of the runs (57 min). The effects of irradiation power and sonication duration are shown in Table 1. The differences in rates for both of these variables are relatively small and the final SO₄²⁻ concentration is relatively unaffected by these changes in conditions. At a constant power, with varying duration of sonication, 10 s appears to be the optimal duration, with slightly lower rates observed at 5 and 20 s. Maintaining the sonication duration at 10 s and varying the power between 28.7 and 38.3 W cm⁻² gives a rate increase of 30%.

Also listed in Table 1, and shown in Fig. 8, are the rates with and without sonication when the initial SO₄²⁻ concentration is increased to 15,200 mg L⁻¹. Here, the precipitation is very rapid, and whilst sonication does appear to increase the rate still further, the time requirement for the analysis means that we were only able to observe the end of the reaction. We also looked at the situation where initial SO₄²⁻ concentration was reduced to 4000 mg L⁻¹. Here, there is virtually no difference between the sonicated and non-sonicated sample. The precipitation reaction appears more complex at this concentration: there is an initial decrease in SO₄²⁻ concentration followed by a levelling off and then a further reduction that appears to be accelerating in rate towards the end of the experiment. This data was not a good fit to a single exponential, as was observed for the experiments at higher concentrations; therefore no rates were calculated (Fig. 9).

Finally, we investigated the effect of delaying the commencement of sonication until a point later in the run for a mixture containing an initial SO₄²⁻ concentration of 7200 mg L⁻¹. Fig. 10 shows that there is a rapid decrease in SO₄²⁻ concentration subsequent to a 10 s sonication that is applied at a delayed time of 7 min 30 s.

4. Discussion

From literature studies involving ultrasonic irradiation of supersaturated solutions, there is strong evidence that enhanced precipitation occurs as a result of cavitation-induced nucleation [17]. Whilst the precise mechanism by which nucleation is promoted remains contested [17], the effect usually results in reduced induction times prior to the observation of precipitation [7,17]. Nevertheless, there is evidence of other factors being involved, with Nishida showing that ultrasound-induced mixing effects, so called ‘macrostreaming’, is the most significant factor in determining the rate of precipitation of calcium carbonate from supersaturated solutions [9]. This conclusion was reached from the observation that altering the composition of dissolved gases in the supersaturated solutions had no effect on the rate of precipitation when irradiated with ultrasound. Such an observation is not consistent with cavitation being the primary factor. Precipitation rates were instead found to correlate with the effectiveness of mixing.

Our results show that for applications where the precipitant is a sparingly soluble solid, a different mechanism to either of the above two proposals is likely. Precipitation rate, particle size and SEM analysis data show strong evidence that under the conditions used in this study, the primary mode of action for ultrasound is to disaggregate the calcium hydroxide particles; thus increasing the extent of the solid/aqueous interface, thereby increasing its dissolution rate and the availability of calcium ions to participate in the precipitation reaction. Moreover, from the particle size analysis it
is evident that the smaller size fractions are achieved immediately upon application of ultrasound. The increased rate of availability of calcium ions can be inferred from the proxy observation of pH, which is found to increase at a greater rate in the presence of ultrasound.

The mode of action for disaggregation is likely to be the cavitation-induced microjets that result from asymmetric collapse of cavitation bubbles in the vicinity of solid surfaces. [18–20]. Such jets possess tremendous velocities (ca. 400 km h$^{-1}$) and can act either directly or can induce particles to move at similar speeds, resulting in high speed particle–particle collisions. These processes have been shown to reduce the overall particle size [19], as well as causing pitting and scouring of solid surfaces [20].

The effects can be achieved with sonication durations as low as 10 s at a power density of 33.5 W cm$^{-2}$. From our initial optimization studies it is likely that longer durations and higher powers may act to promote redissolution of the calcium sulfate, whilst at lower powers and durations, insufficient disaggregation of the calcium hydroxide occurs.

We have used batch mode in these experiments, whereas in practical applications continuous mode is more likely. In such configurations, lime treated effluent is passed through a flow cell that brings it into direct contact with cone-shaped active region formed below the sonotrode [22]. In our batch-mode experimental configuration, the contents of the beaker must circulate through the active region. Nevertheless, there is very little difference observed in precipitation rate between 5 and 20 s sonication duration, suggesting that the mixing time is not rate limiting.

Finally, it is important to note that precipitation and crystallization are highly complex processes that are influenced by other factors.
components within the system and the resultant competing equilibria. For example, the presence of significant concentrations of metal ions in industrial wastewater streams can have a marked effect, as observed by Gominsek et al. in their study of sulfate precipitation from sulfuric acid by lime in a continuous process [13]. They found that over a period of 24 h, competing equilibria acted to alter the course of supersaturation compared to pure sulfuric acid, reducing overall removal. In this context, sonication may provide for a more consistent process by accelerating the precipitation rate of the SO$_4^{2-}$ at the expense of longer-term deleterious processes.

5. Conclusions

In this study we have shown that ultrasound causes a significant increase in the rate of SO$_4^{2-}$ precipitation during the reaction between sulfuric acid and calcium hydroxide. Nevertheless, it is notable that ultrasound appears to have no significant effect on either the induction period, nor on the final equilibrium concentration of SO$_4^{2-}$.

Ultrasound is likely to act by disaggregation of the calcium hydroxide particles so that there is a greater solid–liquid interface, resulting in a faster dissolution rate and more readily available calcium ions. This is supported by particle size and SEM analysis. These effects can be achieved with sonication durations as low as 10 s.

The effect of sonication is dependent on the initial SO$_4^{2-}$ concentration, with the greatest effect observed for an initial concentration of 7200 mg L$^{-1}$. At higher concentrations the precipitation rate is still influenced by sonication, but as the non-sonicated reaction is very rapid, sonication is unlikely to be of benefit. For lower concentrations, sonication appears not to be very effective, at least over the time scales used in this study.

Ultrasound appears to have no affect on crystal morphology in this study, though it does act to break up the larger planar crystal structures. This has a negative impact on the rate of sedimentation compared to non-sonicated samples, as might be expected, though with use of a flocculent, this effect is diminished and the final settling volume is unaffected.

This patented technology, developed by Integrated Effluent Solutions Ltd, UK, is currently being used in full scale treatment plants [23].
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