



Research article

Treatment of a highly-concentrated sulphate-rich synthetic wastewater using calcium hydroxide in a fluidised bed crystallizer

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ARTICLE INFO

Article history:

Received 26 May 2017

Received in revised form

30 August 2017

Accepted 21 September 2017

Keywords:

Desalination
 Fluidised bed crystallizer
 Precipitation
 Gypsum
 Magnesium hydroxide
 Saline wastewater
 Sludge

ABSTRACT

This study aimed to investigate factors that affect the conversion of sulphates and magnesium, and the recovery of gypsum and magnesium hydroxide in the neutralization of a sulphate rich stream using calcium hydroxide, in a laboratory scale seeded fluidised bed crystallizer. Particular focus was on reducing the precipitated fines that escaped with the treated water, through the use of seeds, while removing as much sulphate-compounds from the waste stream as possible. The composition of the total sulphate salts was as follows: 80% magnesium sulphate, calcium sulphate remaining at its saturation concentration (1.5 g/L), with the remainder being sodium sulphate based on typical reverse osmosis retentate concentrations ranging from 1.5 – 120 g/L of total sulphate salts. The fluidised bed crystallizer, using silica seeds, was found to be effective at reducing the formation of gypsum and magnesium hydroxide fines by almost half. Feed concentrations of 35 g/L of total salts yielded better sulphate conversions ($\pm 75\%$), compared to a feed concentration of 8 g/L ($\pm 30\%$). It was possible to remove 99% of the magnesium in the saline wastewater stream using a calcium to sulphate ratio of 1:1 for feed concentrations of 15 g/L and higher. Excess calcium hydroxide suspension improved sulphate conversions.

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1. Introduction

Saline wastewaters which are rich in magnesium, sodium and calcium sulphates, primarily emanate from industrial operations such as mining, metal plating, smelting and pigment manufacturing (van Hille et al., 2005) as well as seawater (Ayoub et al., 2017). In fact, currently, the four most concentrated metals in seawater are Na, Mg and Ca, which are commercially extracted as Cl^- , SO_4^{2-} and CO_3^{2-} with Mg extracted as MgO (Vigneswara et al., 2017). Ayoub et al. (2017) have confirmed similar concentration trends for these metals. Such saline wastewaters are typically passed through a reverse osmosis membrane resulting in clean water and a highly-concentrated retentate stream (Ayoub et al., 2017; Khedr, 2012). While reverse osmosis treatment has been found to be effective, discharging the highly-concentrated retentate without pre-treatment is detrimental to the environment and substantial investment has been made towards developing effective treatment and disposal methods. Among the most common treatment methods, is metal removal via precipitation, through the

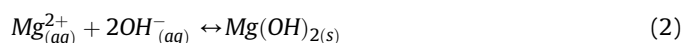
addition of lime or caustic soda (van Hille et al., 2005). However, this results in the formation of very fine suspended solids, in other words, the generation of large quantities of sludge with poor dewatering characteristics (Fajtl et al., 2002; Yehya et al., 2015). Thus, separation of the precipitate from the treated stream is difficult, thereby increasing handling and disposal costs (van Hille et al., 2005; Fajtl et al., 2002; Karidakis et al., 2005). Additionally, the presence of other components in solution may lead to a mixed precipitate, which limits its applicability for reuse. These disadvantages have led to further research into more efficient precipitation processes. A particular technological innovation is the use of seeded precipitation in a fluidised bed crystallizer. Crystallisation in fluidised bed reactors have been extensively used in industry for the softening of drinking water (Aldaco et al., 2007) as well as heavy metal (Zhou et al., 1999) and phosphate removal from saline wastewaters (Seckler, 1994). Omar et al. (2010) found fluidised bed crystallizers to be a feasible process for calcium sulphate scale removal in seawater desalination.

The use of fluidised bed crystallizers allows for controlled precipitation and has many advantages over conventional stirred tank crystallizers, like the elimination of significant impeller crystal collisions and the ability to harvest pellets that migrate to lower regions of the reactor once they reach a size that is too heavy to

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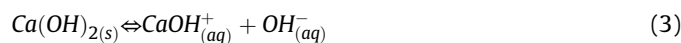
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fluidize. Fluidised bed crystallizers use seeds to minimise the generation of fine particles by providing a large surface area for crystal growth or deposition by lowering the surface energy requirements, compared to homogenous nucleation, that is, nucleation in the absence of a solid (Mullin, 2001). As the precipitation reaction proceeds, the seeding material becomes covered, either through growth, attachment or simply entrained with gypsum and magnesium hydroxide and subsequently migrates to the bottom of the reactor. This allows for the precipitating compounds to be separated from the treated stream in the form of pellets, which can be harvested. The formation of gypsum and magnesium hydroxide is presented in Equations (1) and (2).



The mechanism of 'growth' has been proven to occur in low-concentration systems of 150 mg/L Nickel (Guillard and Lewis, 2001); 5–100 mg/L Phosphorous (Seckler, 1994); 3000 mg/L total metals (Zhou et al., 1999); 3557 mg/L NiSO₄ (Wilms et al., 1988) and 5500 mg/L (Tai et al., 1999). In these cases, supersaturation (S) is relatively low thus promoting nucleation on the seed surface, which facilitates the solid-liquid separation process and avoids large volumes of sludge streams (Guillard and Lewis, 2001; Heffels and Kind, 1999).

While most studies conducted using fluidised bed crystallizers focused on low concentration systems, the application of such crystallizers in the treatment of a highly-concentrated system has not been explored yet. The precipitation of sparingly soluble compounds from highly-concentrated saline wastewater is associated with high supersaturation resulting in the formation of fines. In this instance, the precipitate is retained in the fluidised bed/reactor through agglomeration and growth mechanisms which allow crystals to attach on to the seed surface, reducing the amount of fines lost with the residual treated stream. Nevertheless, it is still necessary to minimise the formation of these fines and this may be achieved by controlling supersaturation through the addition of a base reagent of low solubility as a suspension (Seckler, 1994; Kitamura et al., 2002), for example, milk of lime (calcium hydroxide (Ca(OH)₂)). Equations (3) and (4) show the release of calcium and hydroxyl ions during the dissolution process.



The use of a suspension ensures a controlled release of ions as the reaction proceeds to maintain the equilibrium concentration in solution, thereby controlling the supersaturation. This avoids zones of high supersaturation, for example, at reactor inlets or with instances where mixing is imperfect (Seckler, 1994; Guillard and Lewis, 2001), but does not entirely address high zones of supersaturation around dissolving particles in some instances. Moreover, limiting the supply of reacting ions is not without its trade-offs and may hinder the reaction if ions are not supplied effectively.

This study investigated the feasibility of using a seeded fluidised bed crystallizer for sulphate and magnesium removal from a multicomponent stream, rich in magnesium and sodium sulphate, using a calcium hydroxide suspension. The presence of sodium and magnesium in an aqueous system can introduce many complications (Ahmed et al., 2014). According to Mullin (2001), these additional components alter solution properties, diffusion coefficients or the structure of the solution. The solubility of gypsum

is known to fluctuate with increasing concentrations of sodium sulphate (Popovic et al., 2011). This behaviour is due to electrostatic effects, speciation and the common ion effect.

The study focused on the minimization of fines while removing as much of the magnesium and sulphate in the feed stream as possible. Particular focus was on the effect of the feed concentration and the ratio of calcium hydroxide fed on the conversion of sulphates and magnesium to gypsum and magnesium hydroxide respectively, as well as the amount of fines formed.

2. Materials and methods

2.1. Thermodynamic modelling

OLI Systems Stream Analyser™ was used to model the aqueous chemistry and predict the phases in the multicomponent system as well as the maximum obtainable conversions. The software makes use of thermodynamic equations to predict parameters such as activity coefficients using the electrolyte NRTL model, with the extended form of Bromley equation to generate limited or unknown data. Molecule-molecule and ion-molecule interactions are modelled using the Pitzer model, while standard state properties are approximated with the Helgeson-Kirkham-Flowers Equation of State. The Soave Redlich-Kwong Equation of State is used to determine fugacity coefficients of non-ideal states (OLI manual, 2015).

2.2. Reactor design

All experiments were conducted using a Perspex laboratory scale fluidised bed crystallizer filled with seeding material (Silica, 200–300 μm, \bar{x} = 250 μm) to a height of 0.3 m, shown in Fig. 1. A bed height to reactor diameter ratio of above 10 was chosen for good fluidisation of the Group B (Geldart's classification of Powders) seeding material (Shaul et al., 2012). The bottom of the reactor was filled with glass beads (0.005 m diameter) to a height of 0.05 m to disperse the influent stream and to avoid channelling in the bed. The saline solution was stored in a plastic 25 L tank which was continuously agitated to eradicate concentration gradients. A feed flowrate of 200 ml/min was chosen as it ensured good fluidisation of the bed and a residence time of around 2 min in each experiment. Product harvesting was done by intermittently opening a ball valve through which large particles, which have migrated to the bottom of the bed, exit provided there is sufficient force to keep the bed fluidised.

2.3. Reagents

The feed concentration was based on typical salt concentrations emanating from desalination operations after reverse osmosis treatment, where calcium sulphate is usually at its saturation concentration. In water treatment, concentration is of particular importance to determine the viability and effectiveness of precipitation as a treatment method. From a crystallisation point of view, concentration is important due to its direct relation to the driving force of crystallisation and thus nucleation and growth mechanisms. Practically, the concentration of the saline wastewater to be treated is hardly fixed and investigating its effect on conversion and the formation of fines is critical. Synthetic solutions of total salt concentrations varying from 1.5 to 120 g/L were prepared using analytical grade chemicals (Merck). These total salt concentrations were chosen based on typical reverse osmosis reject concentrations (Khedr, 2012). To simulate a realistic case study, the composition of the total sulphate salts was as follows: 80% magnesium sulphate, calcium sulphate remaining at its saturation concentration (1.5 g/L),

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