Chemical Engineering Science 142 (2016) 23–31

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

The controlled growth of calcium sulfate dihydrate (gypsum) in aqueous solution using the inhibition effect of a bubble column evaporator

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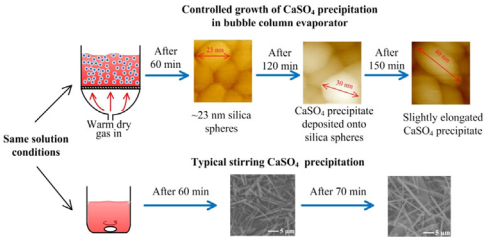
HIGHLIGHTS

- Novel approach to control precipitation using a bubble column evaporator (BCE).
- Inhibition of precipitation observed within a BCE compared to normal stirring.
- Characterization of $CaSO_4$ precipitates deposited onto 23 nm silica spheres in a BCE.
- The BCE process may be used for the production of fine particles of controlled size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form
19 November 2015
Accepted 29 November 2015
Available online 9 December 2015

Keywords:
Calcium sulfate dihydrate
Growth control
Aqueous precipitation
Bubble column evaporator
Surface charge density

ABSTRACT

Chemical precipitation is a widely used method to synthesize sparingly soluble salts for inorganic materials production. A bubble column evaporator (BCE) process was used to precipitate calcium sulfate (as $CaSO_4 \cdot 2H_2O$) from the reaction of calcium chloride and potassium sulfate solutions, at different degrees of supersaturation. In the BCE system, fine bubbles are continuously produced as a warm dry gas is pumped into a column of solution through a porous sinter. This process was used here as the basis for a new approach to control precipitation with uniform mixing and continuous concentration through rapid water vapor transfer. In this study it was found that the BCE process, compared to simple stirring and even the quiescent solution, had a significant inhibition effect on the induction of precipitation and reduced the growth rate of the precipitate. This precipitation control facilitates the collection of particles over a wide range from nanometer to micrometer size. In the BCE process, the early stage of $CaSO_4$ precipitated onto the surface of nano-sized silica spheres was characterized using dynamic light scattering, zeta potential analysis and atomic force microscopy imaging, which indicated that a coating was produced on the silica surface. The inhibition effect observed with the BCE process suggests that it could be used for controlled precipitate growth and also for the de-watering or concentration of industrial wastewater prior to disposal.

1. Introduction

Precipitation from aqueous salt solutions is one of the most basic processes in chemistry but has often been neglected as a method for the production of fine inorganic particles (Demopoulos, 2009). Demand for fine inorganic particles in the micron and submicron range is increasing for use in a wide range of industries, including

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http://dx.doi.org/10.1016/j.ces.2015.11.027
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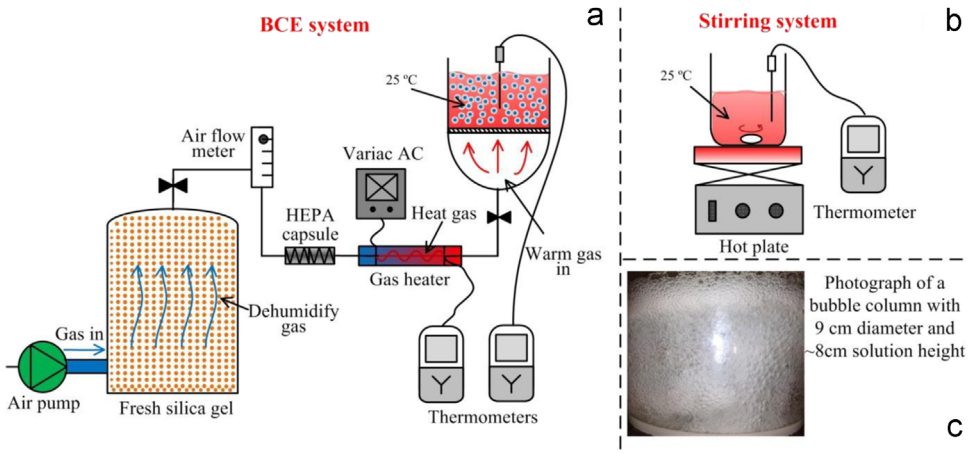

Fig. 1. Schematic diagram of BCE (a) and stirring (b) systems for $CaSO_4$ precipitation at 25 °C, and a photograph of a bubble column for mixing 0.04 M $CaCl_2$ and 0.04 M K_2SO_4 (c).

ceramics, catalysts, pharmaceuticals and cosmetics (Tóth et al., 2005). The design and production of fine particles with controlled particle properties, say particle size, nucleation and growth rate, morphology etc., are important for both scientific studies and numerous industrial applications (Bakhbakhi et al., 2013). Fine inorganic particles are conventionally and industrially formed by a range of processes such as spray drying, fluid grinding, fluidised-bed spray, solvent evaporation and lyophilisation (Shekunov and York, 2000; Subramaniam et al., 1997; Tan and Borsadia, 2001; Ye and Wai, 2003). However, these methods often produce relatively poor particle properties and have high energy requirements. There are other experimental studies on the production of fine inorganic particles precipitated from aqueous solutions, which are mostly achieved by creating supersaturated conditions, such as, by the addition of other components (normally organic soluble chemicals) to change solubilities (Barata and Serrano, 1996; Mullin et al., 1989; Najdanovic-Visak et al., 2007; Tóth et al., 2005), or by stirring or simply mixing two aqueous reagents (Giorgi et al., 2005; Kawase and Miura, 2007; Voinescu et al., 2007; Wang et al., 2012). These solution processes typically produce fine particles in the μm size range.

Calcium sulfate ($CaSO_4$) or calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) are common minerals precipitated from seawater and natural brines, and in practice, they are also often a problem in the form of scale deposits produced in many industrial processes, such as in water treatment and desalination (Cowan and Weintritt, 1976). These precipitates have been studied for precipitation kinetics (He et al., 1994a, 1994b; Klepetsanis and Koutsoukos, 1991; Smith and Sweett, 1971), morphology and characterization (Hazra et al., 2014; Tiemann et al., 2002; Wang et al., 2012) by a few researchers. The control of $CaSO_4$ precipitation over the range from nanometers to microns in aqueous solutions, however, has not yet been studied due to the typically rapid growth observed after the induction of precipitation.

In this work, we report a novel process of $CaSO_4$ precipitation in a controlled manner using a bubble column evaporator (BCE), which combined vigorous mixing with uniform solute concentration to facilitate a more controlled precipitation process compared to a typical stirring system. Some types of concentrated salt solutions have unexpected effects on the coalescence inhibition of bubbles (Craig et al., 1993a, 1993b), which has facilitated the BCE process by the controlled production of a high density of fine bubbles. 1–3 mm diameter bubbles created by this type of column are saturated by water vapor within a few tenths of a second (Leifer et al., 2000). The combination of bubble coalescence inhibition and rapid water vapor transfer can be used as the basis for a novel approach to produce particles over a wide range of size in a controlled manner. Also, the BCE process has the possibility of several flexible control variables, such as flowrate, gas type, gas humidity and inlet gas temperature (Fan and Pashley, 2015; Fan et al., 2014; Francis and Pashley, 2009) to help produce optimum conditions.

The BCE method was found to have an inhibition effect on the precipitation of $CaSO_4$ and reduce its rate of growth, in supersaturated solutions, which facilitates the collection of particles over a wide range from nanometer to micrometer size. Based on the results obtained in this study, the BCE process might also be used for concentrating solutes in wastewater, whilst reducing precipitation.

2. Materials and methods

2.1. Materials

The salts $CaCl_2$ and K_2SO_4 used in these experiments were analytical reagents with purity levels of $\geq 99\%$ and were purchased from Sigma-Aldrich. Double distilled water was used to prepare the salt solutions and purified bottled drinking water, Select Mountain Spring, was used for a low particle count comparison. At room temperature, the distilled water had a conductivity < 2.0 μS/cm and a natural equilibrium pH of 5.7. All concentrations are given in molarity (M) units at around room temperature. Plain SiO_2 nanospheres (23 nm in diameter, coefficient of variation $< 15\%$) and microspheres (1.5 μm in diameter) that were purchased from Corpuscular were used to nucleate $CaSO_4$ precipitates.

2.2. Precipitation processes

A BCE process and a stirring process were used in these experiments to study $CaSO_4$ precipitation at around 25 °C, as shown in Fig. 1, which also gives a photograph of bubbles in the mixed $CaCl_2$ and K_2SO_4 solutions. For the BCE process, the air was continuously pumped through a large quantity of fresh silica gel (Ajax Fine Chem) to remove water vapor. The controlled inlet flow rate ($\sim$10 L/min) was also monitored using a BOC flowmeter (0–15 L/min), which was placed after the desiccators (fresh silica gel), and then the air was filtered using a Whatman large High Efficiency Particulate Air (HEPA) filter capsule which can retain 99% of all particles ≥ 0.3 μm in the inlet air. A Tempo air heater was used to heat the air to a stable inlet gas temperature, as the heater was controlled by a digital vari-AC power supply and was monitored by a thermocouple (TM-82N Tenmars). The controlled temperature air finally entered into the bubble column where the salt solutions were maintained at around 25 °C, which was monitored by a