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The use of ultrasound to enhance crystallization of minerals from concentrated saline effluent

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Abstract

Many effluent treatment processes result in a concentrated brine solution that requires disposal. Bulk crystallisation of the salt can facilitate this disposal, by providing a solid that can be more readily transported. In this presentation, we consider the use of ultrasound to assist in initiating the crystallisation of salt from saline effluent sourced from the Australian dairy industry. The effluent has already been concentrated to 22 or 30 wt% total solids, these being principally sodium chloride, but with some calcium phosphate and lactose. The precipitation follows reverse solubility behaviour with respect to temperature, with the shortest induction times at the highest temperature. This reflects the low solubility of the calcium phosphate salts, which precipitate first. Ultrasound can significantly reduce the time required to induce crystallisation. The use of a higher power produces a greater reduction in crystallisation time, relative to a lower power at the same energy density. Further, the use of two pulses of ultrasound during the induction period, also shortens this induction period, relative to the same energy application as a single pulse. Indeed, using a double pulse reduces the induction time to around 30 minutes, relative to 2.6 hours without ultrasound. Ultrasound also influences the crystal morphology, with needle like crystals only appearing when this is utilised. However, the ultrasound cannot improve the crystal yield, which is limited by the relative humidity of the atmosphere above the crystallising solution.

Keywords: sonocrystallisation; dairy; sodium chloride; calcium phosphate

1 Introduction

The crystallisation of salts from a solution follows two fundamental steps: nucleation followed by crystal growth. Nucleation is the first stage of solid formation, where the clusters of molecules form an unstable equilibrium with the surrounding solution. A nucleus is defined as the minimum number of molecules required to form an independent new phase [1]. Primary nucleation can either be homogeneous in the absence of a solid surface or heterogeneous when it involves a foreign surface [2-4] such as a container wall, impeller or surface. Practically, homogenous nucleation is an uncommon process which only takes place at very high levels of supersaturation. Heterogeneous nucleation can happen more rapidly and at lower supersaturation levels. With increasing supersaturation level, i.e. increasing chemical potential difference between solid and liquid phases, the driving force for nucleation increases, resulting in a decrease in induction time. The formation of the first supernucleus in the solution brings the system out of the metastable zone equilibrium [5-7].

Secondary nucleation occurs when the desired solid is added to the system, e.g., by crystal seeding. Nucleation occurs on the seed templates at lower supersaturation levels. Collision breeding is also classified as secondary nucleation, where crystal-crystal or crystal-equipment collisions create additional surface to accommodate crystal growth [2, 8].

Nuclei, or small crystals, require supersaturation concentrations to accommodate crystal growth. During the crystal growth phase the growth unit or monomer diffuses toward the surfaces of growing nuclei. Clusters are collections of growth units. The simplest nucleation theory (Classical Nucleation Theory) explains that formation of the more stable form (solid) decreases the volume free energy ΔG_V. The formation of clusters is dictated by the net free energy ΔG, which depends on two competing factors ΔG_V and ΔG_s, which is the excess free energy based upon the surface interfacial tension (γ) and radius of the particle (r). Smaller size crystals with higher solubility than large crystals may exist in equilibrium with the supersaturated solution. Where crystals reach a critical size, spontaneous solid formation takes place at the macroscopic scale. The time taken for formation of detectable crystal from supersaturation conditions is defined as the induction time [9-11].

$$\boldsymbol{\Delta G = \Delta G_V + \Delta G_s = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v} \quad (1)$$

In a simplified system of stationary nucleation of a single nucleus, the induction time can be written as a function of nucleation rate as Equation 2.

$$\boldsymbol{t_i = \frac{1}{JV}} \quad (2)$$

$$\boldsymbol{t_i = \frac{1}{JV} + \frac{3\alpha_v}{(\pi g^3 J)^{0.25}}} \quad (3)$$

For a more complex system with a number of supernuclei,Equation 3 is required, where J is the nucleation rate, V is the constant volume and g is the time independent growth rate [5, 6]. The history of the solution and the rate of reaching a supersaturation condition also affects the nucleation rate [12].

Compared to nucleation, crystal growth requires a lower supersaturation driving force, i.e., chemical potential difference between the solution and the crystal. Such crystal growth follows classical mass transfer mechanisms [13]. The first stage is mass transfer of a growth unit in the solution to the surface of the solid through diffusion or convection. Crystal growth behaviour also depends on impurities in the solution. Impurities can be unavoidable yet can also be purposely added to control precipitation. Generally the presence of impurities retards the growth rate of the desirable crystal [14]. Growth decreases with increasing impurities adsorbed on the surface of the crystal. This effect is more prominent at low supersaturation levels in which growth rate is relatively slow. This is often represented as the *impurity factor* [15].

The benefits of ultrasound to enhance both nucleation and crystal growth have been widely reported. Guo et al. 2005 [16] shows that insonation (application of ultrasound) shortens the induction time and narrows the metastable region. It is argued that the ultrasound improves the mass-transfer coefficient. According to classical nucleation theory, the diffusion coefficient is inversely proportional to induction time. Thus, insonation shortens the induction time at a given superaturation ratio [16, 17]. The effect on crystal growth and product recovery has also been investigated [18-26]. Crystal habit, morphology and size distribution can be altered by varying insonation parameters [27-31]. Insonation to aid the crystallisation process can be introduced to the system as intermittent pulses, short bursts or through continuous sonication [26, 29]. Research into the fundamental mechanisms of sonocrystallisation is ongoing. Arends et al. 2003 [32] have patented sononucleation of fat in the absence of cavitation, yet most researchers claim that sonocrystallisation

Cavitation is thought to affect crystallisation through several mechanisms. Focusing on the nucleation stage (sononucleation), the first mechanism relates to bubble collapse. The energy released during collapse events allows the nucleation energy barrier to be overcome [29, 33] and the localized temperature surge alters the supersaturation level. For cooling crystallisation, this is counter-intuitive as the solubility and supersaturation limits increase with increasing temperature. However some researchers [3, 29, 34] suggested that with localized extremes temperature, the rate of cooling is also enhanced (107-1010 K/s) [3] which results in faster nucleation. In sono-nucleation of water-ice Cogne et al. 2016 shows that nucleation could occur at a higher liquid temperature for a specific acoustic pressure range. It is also argued that the zone of high pressure is much larger than zone of high temperature. Thus, the possibility of nucleation at higher temperature is also influenced by the size of the bubbles and the pressure.

Another mechanism relies on the role of cavitation bubbles as nucleation sites [35, 36] which substitutes for the necessity of seeding [27], it is thus possible to conduct primary nucleation in a particle free solution at a lower supersaturation level system.

The application of ultrasound also improves mass transfer and maintains system homogeneity, especially in batch processes [37, 38]. Some authors argue that ultrasound has a more pronounced effect at low supersaturation levels through mass transfer enhancement [16]. On the other hand, Virone et al. 2006 [17] state that acoustic cavitation increases the reproducibility of nucleation irrespective of the initial supersaturation. With discrete or continuous insonation, microturbulence and shock waves are generated, enhancing convection in the bulk phase.

Nalajala et al. 2011 [39] argue that shock waves and microturbulence dictate nucleation rate and nucleus growth respectively, with the effect of the former more apparent than the latter.

In the present work, we apply low power ultrasound to reduce the induction time for the crystallisation of salts from concentrated dairy effluent. Ultimately, this facilitates disposal of the effluent and also many facilitate recycling of some salts into the dairy process.

2 Materials and Methods

Isopropyl alcohol (≥ 99.7%) was purchased from Merck. Saline dairy effluent in the form of salty whey permeate was obtained from a dairy factory within Victoria, Australia. This effluent contains high concentrations of sodium chloride, but also smaller concentrations of calcium phosphate, as well as lactate and citrate salts. This effluent was concentrated further using membrane distillation to either 22 or 30 wt% total dissolved salts, according to a previously described technique[40].

Crystallisation of concentrated saline effluent was conducted in a 150ml cell with a double walled cooling jacket. All experiments were conducted using the same vessel and configuration as the liquid height can greatly affect the ultrasound intensity delivered to the liquid [41, 42]. For all experiments, 100g of concentrated saline effluent was introduced into the crystallisation cell directly from the membrane distillation feed tank. An online turbidity probe was utilised to monitor the onset of crystallisation with the data recorded every minute.

A Digital sonifier (Branson Ultrasonic Corporation, Nominal Power 400W, frequency 20 kHz) was utilised, with the actual power drawn was measured using a power meter fixed to the instrument power supply (ARLEC).

Ultrasound was applied as zero, one or two short pulses, from 3 to 20 seconds in duration. When two pulses were used, these were spaced ten minutes apart. The concentrate was then left to crystallize under constant temperature and stirring conditions.

3 Results and Discussion

The cavitation generated through the application of ultrasound shortens the induction time across the temperature range tested (Figure 1). These effects probably reflect bubbles generated in the solution acting as a foreign surface to facilitate heterogeneous crystallisation [36, 43]. At the low ultrasonic frequency used(20 kHz), the bubble collapse is intense and provides extra energy to overcome the nucleation energy barrier. The literature indicates that the cavitation intensity is greater at lower temperatures[41]. However, there is no evidence of a greater effect at lower temperatures in this study. Nonetheless, for the same acoustic energy density (15 J/kg) and temperature (50^{o}C), the effect of ultrasound is more pronounced at 22 wt% total solids, causing the induction time to fall from 12 to 1.5 h.

Increasing the energy density from 3.7 to 15 J/g by increasing duration of insonation has no effect in altering the induction time (Figure 1). Zamanipoor et al. [44] and Nii et al. [45] also claims that low frequency ultrasound has Little effect upon crystal growth rate. On the contrary, the effect of power density to shorten the induction time is paramount. With constant energy

density of 8 J/g , reduction of induction time is observed from 3.3 hours down to 1.7 hours by increasing the power from 18 to 75Watt (Figure 2). This result agrees with the work of Dincer et al [22], who observed a 40% reduction in induction time for a lactose solution by supplying a six fold increase in power. Kordylla et al [46] also claims that the power supplied determines the formation of the first nuclei.

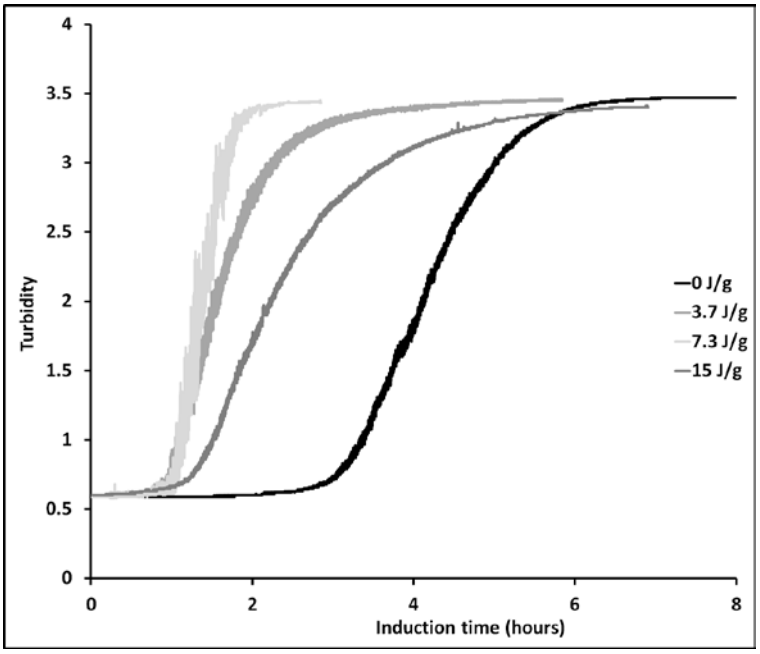

Figure 1: Turbidity measurements showing the onset of crystallisation. Experiments conducted without ultrasound (0 J/g) and with a single pulse of ultrasound at variable energy density, generated by increasing the length of the acoustic pulse (Initial solids 30 wt%, 50°C)

The use of a second short pulse of ultrasound, ten minutes after the first, had a significant effect on the induction time (Figure 3). At 50°C and a total energy supply of 7.3 and 15 J/g, the induction time was reduced from 1.2 hours to 0.8 hours. At 3.7 J/g and 50°C, the data for the single and double pulse cases converged, perhaps suggesting that this is the minimum energy threshold required for the ultrasound to be effective.

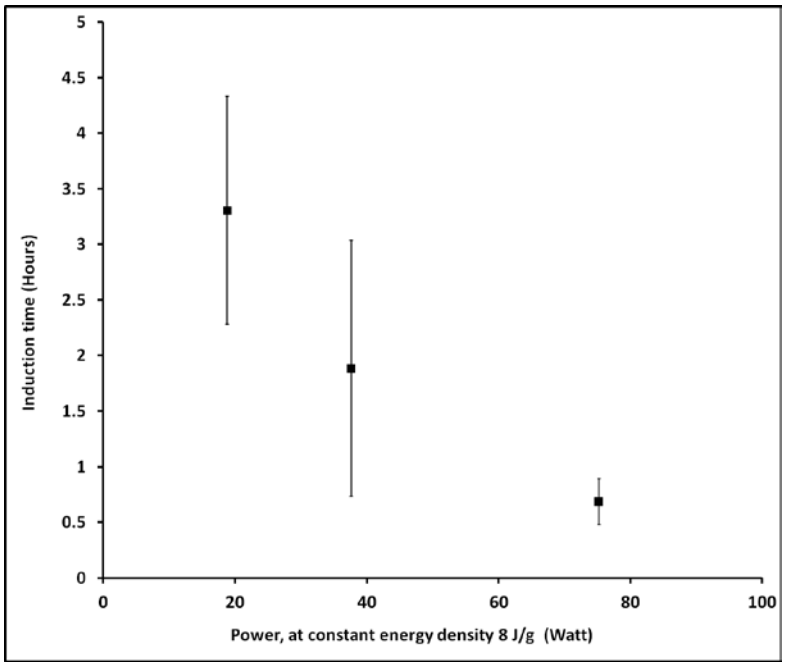

Figure 2. Induction time with respect to power conducted at 50°C at and constant energy density 8 J/g (initial solids 30wt %)

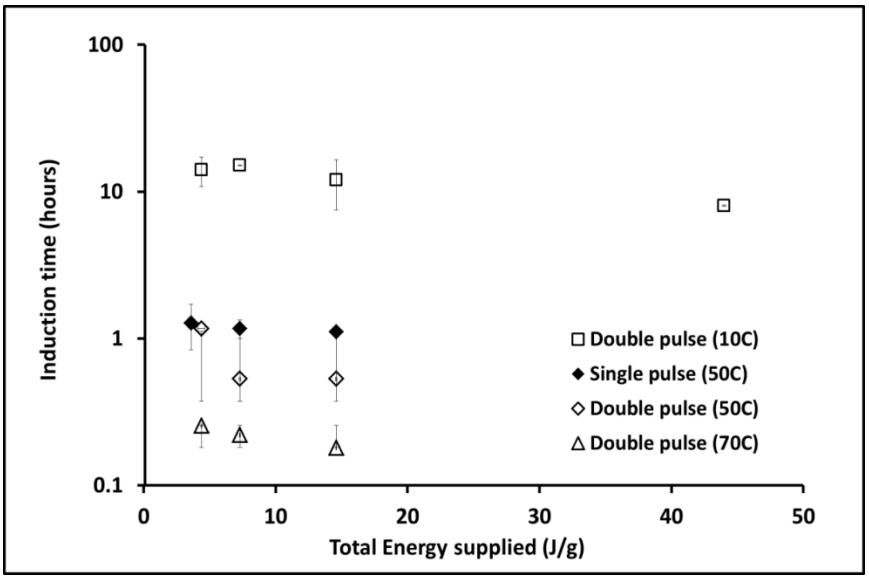

Figure 3. Induction time for single and double pulse application. The energy quoted is the total supplied across both pulses when two pulses are used (Initial solids 30 wt%).

4 Conclusions

Low frequency ultrasound is shown to be effective in reducing the induction time of salts from concentrated saline effluent. The best results are achieved by the use of two short pulses spaced ten minutes apart. The use of high acoustic power levels is important, whereas prolonging the length of the acoustic pulse has no effect.

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