



# Crystallisation of minerals from concentrated saline dairy effluent



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## ABSTRACT

An understanding of crystallisation within saline effluents is important for the design of both brine crystallisers and brine disposal ponds. In this work, crystallisation of a saline effluent concentrate from the Australian dairy industry has been examined at 22 wt% and 30 wt% total solids and at temperatures between 10 and 70 °C. The precipitation occurs more rapidly at higher temperatures. This trend is dictated by precipitation of calcium phosphate salts, albeit the major constituents of the mixture are NaCl and lactose. The crystallisation induction time can be shortened by introducing cavitation induced by ultrasound. In particular, the use of two short acoustic pulses between 3.7 J/g and 16 J/g at 20 kHz spaced ten minutes apart has maximum impact upon both induction time and crystal size. It is believed that the first ultrasound pulse either generates new nuclei or enhances the mass transfer of solute toward the surface of sub-micron growing crystals. Conversely, the second pulse disrupts the growing crystals and forms secondary nuclei. The ultrasound cannot shift the solution equilibrium and so is not able to improve the low crystal yield. To increase this total yield, further evaporation is necessary. The work provides direction to personnel in the dairy industry of the feasibility of brine crystallisation with respect to energy demand and solid recovery.

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## 1. Introduction

The dairy industry is a major rural industry in Australia and generates 11 GL/y of liquid effluent (Blaschek et al., 2007). This effluent predominantly comprises waste from cleaning-in-place processes (CIP) and the salty whey by-product from hard cheese manufacturing. While traditionally, this waste has been handled by municipal water authorities; their continuing ability to do so is declining due to environmental constraints and increasing costs. This means that dairy companies can be forced to treat such saline waste on site; either through brine evaporators and crystallisers or the use of brine evaporation ponds. However, the efficiency of these units is limited by the energy consumption, the mass transfer driving force and fouling deposition. A better understanding of the crystallisation of salts from these wastes could allow crystallisation at lower salt concentrations, leading to energy reduction; or alternatively could assist in fouling mitigation.

The crystallisation process follows a number of fundamental steps, including nucleation, crystal growth, agglomeration and recrystallisation. The crucial driving force for both nucleation and growth is the supersaturation level. This supersaturation condition can be induced by addition of an anti-solvent, solvent evaporation, shifting the pH or by temperature change. Primary nucleation can either be homogeneous, in the absence of a solid surface, or heterogeneous where a foreign surface such as the container wall, impeller or the surface of a membrane is used (Mullin, 2001; Rucroft et al., 2005; Yu et al., 2007). On the contrary, secondary nucleation occurs when a crystal seed presents in the system. In practice, homogenous nucleation is an uncommon process which only takes place at very high levels of supersaturation. On the other hand, heterogeneous nucleation can occur even at low supersaturation levels. The precise nucleation mechanism is often difficult to determine, since many compounds possess a wide metastable zone which leads to large variability. The history of the solution as well as the rate at which the supersaturation condition is reached can all govern the nucleation rate (Mullin, 2001). In salt systems where multiple polymorphs can form, such as when calcium phosphate is present, the dissolution of less stable phases and growth of more

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stable ones (re-crystallisation) also influences the final crystal size distribution.

The ability of ultrasound to reduce the induction time before crystals are observed has been widely investigated (Bund et al., 2007; Bund and Pandit, 2007a; Kordylla et al., 2008; Li et al., 2006, 2003; Ruecroft et al., 2005; Wohlgemuth et al., 2010). Ultrasound creates cavitation bubbles which undergo cycles of compression and growth before collapsing. The implosion of these microbubbles within the solution generates localized extreme pressures and temperatures. It is argued that these extreme conditions can shorten the nucleation time by allowing the nucleation energy barrier to be more readily overcome. The shockwaves generated by the implosion events also enhance the mass transfer of solutes toward the growing nuclei and breaks down crystal aggregates to create more surface area for crystal growth (Wagterveld, 2013). The application of ultrasound can also influence the crystal size distribution, uniformity and morphology.

In the dairy industry, ultrasound has been applied to assist in lactose crystallisation from concentrated solutions and the sweet whey produced from cheese manufacturing (Bund and Pandit, 2007b; Dincer et al., 2014; Kougoulos et al., 2010; Zamanipoor and Mancera, 2014; Zisu et al., 2014). However, the precipitation of minerals from saline dairy effluent has not yet been extensively investigated due to the interference of impurities as well as its low economic value. Saline dairy effluent generated in the industry can contain NaCl at very high concentrations due to the deliberate addition of this salt during the production of hard cheeses. Furthermore, a considerable amount of residual lactose and calcium phosphate is usually present in the mixture. This effluent can be concentrated to a certain level through reverse osmosis, membrane distillation and/or evaporation technologies. However, calcium phosphate precipitation and scaling currently limits the concentration level that can be achieved (Amjad, 2013; Kezia et al., 2015; Rice et al., 2009a, 2009b; Schäfer et al., 1998). Selective crystallisation of the calcium phosphate as an intermediate step would thus allow these processes to further concentrate the effluent. The calcium phosphate may also have value as a food additive. Alternatively, bulk crystallisation of NaCl and calcium phosphate as a mixture would allow more efficient disposal of the solid content following concentration.

This study focuses on the feasibility of precipitating these salts from saline dairy effluents at high concentration. To minimize the energy demand, the feed effluent is first concentrated using membrane distillation at 50 °C. Under these relatively mild conditions, the total dissolved solids concentration that can be achieved is limited to  $\pm 30$  wt%, of which  $\pm 24$ – $25$  wt% is NaCl (Kezia et al., 2015). The effect of low energy density ultrasound pulses and changes in temperature are investigated to shorten the induction time for precipitation and to enhance the solid recovery. The ability to selectively precipitate the calcium salts is also considered.

## 2. Materials and methods

### 2.1. Materials

Purified water (a resistivity greater than 15.5 M $\Omega$ -cm, Millipore) is utilised for all experiments and cleaning processes. Buffer and standard solutions were prepared using double-purified water (resistivity greater than 18.2 M $\Omega$ -cm, Millipore). All chemical reagents utilized were analytical grade, isopropyl alcohol ( $\geq 99.7\%$ ) and sodium chloride (NaCl,  $>99.5\%$ ) were purchased from Merck and tripotassium phosphate, K<sub>3</sub>PO<sub>4</sub> ( $\geq 98\%$ ) was purchased from Sigma Aldrich. Lactose ( $\geq 99.5\%$ ), calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O,  $>99\%$ ) and disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>,

$>99\%$ ) were purchased from Ajax Finechem.

The saline waste effluent was kindly supplied from a dairy factory in Victoria, Australia. The samples were labelled here as B1, B2, B3 and B4 (see Table 1). The streams are derived from salty whey, which is the by-product from the production of various hard cheeses. Specifically, the samples were drawn from the permeate stream of an ultrafiltration unit used to recover saleable protein from the salty whey, and had a titratable acidity of 0.1–0.6 w/v% (pH 3.3–5). Upon arrival in our laboratory, the samples are re-filtered using a 10 kDa ultrafiltration membrane (Koch) for process standardisation, thus removing all residual protein. The effluent is then concentrated using membrane distillation at 50 °C to either 22 wt% or 30 wt% total dissolved solids, according to a previously published procedure (Kezia et al., 2015). An independent concentration process was conducted for each crystallisation experiment and the concentrate was then transferred directly to the crystallisation chamber as soon as the final concentration was achieved. This was done to avoid any crystallisation lag time or the unmonitored formation of solid. The data in Table 2 thus represents the average result and the variation around this (one standard deviation of the data). As the protein was removed, the total organic content can be assumed to be predominantly the disaccharide lactose, with trace amounts of galactose and glucose. The mass ratio of relevant minerals in the solution is provided in Table 3.

Some experiments were also conducted using simulated whey solutions. CaCl<sub>2</sub>·2H<sub>2</sub>O (1, 5 and 10 mM) was mixed with Na<sub>2</sub>HPO<sub>4</sub> (1, 5 and 10 mM) in a 1:1 Ca/P ratio. The ionic strength was adjusted to 0, 1.7 M or 5.1 M by adding NaCl. Lactose (0–0.15 M) was also added in some cases.

### 2.2. Methods

The crystallisation of concentrated saline effluent was conducted in a 150 ml cell with a double walled cooling jacket

**Table 1**  
Composition of the saline effluent samples as received from the factory.

Sample labels	Total dissolved solids (%)	Total ash (%)	Total organic (%)
Batch 1	6.6 $\pm$ 0.1	4.9 $\pm$ 0.3	1.7 $\pm$ 0.3
Batch 2	9.0 $\pm$ 0.3	7.4 $\pm$ 0.1	1.6 $\pm$ 0.2
Batch 3	9.6 $\pm$ 0.1	7.4 $\pm$ 0.6	2.1 $\pm$ 0.6
Batch 4	6.8 $\pm$ 0.5	5.4 $\pm$ 0.4	1.4 $\pm$ 0.1

**Table 2**  
Composition of the saline effluent samples after concentration using membrane distillation.

Sample labels	Total dissolved solids (%)	Total ash (%)	Total organics (%)
Batch 1 (22 wt%)	22.1 $\pm$ 0.5	16.5 $\pm$ 0.9	5.8 $\pm$ 0.4
Batch 1 (30 wt%)	30.3 $\pm$ 1.9	23.9 $\pm$ 2.0	6.4 $\pm$ 0.2
Batch 2	30.1 $\pm$ 0.6	25.4 $\pm$ 0.6	4.7 $\pm$ 0.7
Batch 3	31.1 $\pm$ 1.5	24.3 $\pm$ 1.4	6.8 $\pm$ 1.0
Batch 4	30.1 $\pm$ 1.7	24.0 $\pm$ 0.6	6.1 $\pm$ 0.1

**Table 3**  
Mass ratio of sodium (Na) and phosphorus (P) relative to calcium (Ca) within the saline waste effluent after concentration using membrane distillation.

Sample labels	Na	Ca	P
Batch 1 (22 wt%)	12.6	1	0.43
Batch 1 (30 wt%)	13.1	1	0.41
Batch 2	26.5	1	0.46
Batch 3	16.8	1	0.47
Batch 4	26.3	1	0.65

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