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Solubility of Calcium Phosphate in Concentrated Dairy Effluent Brines

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1 The solubility of calcium phosphate in
2 concentrated dairy effluent brines

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18

19 ABSTRACT

20 The solubility of calcium phosphate in concentrated dairy brine streams is important in
21 understanding mineral scaling on equipment such as membrane modules, evaporators and
22 heat exchangers, and in brine pond operation. In this study, the solubility of calcium
23 phosphate has been assessed in the presence of up to 300 g/L sodium chloride as well as
24 lactose, organic acids and anions at 10°C, 30°C and 50°C. As a neutral molecule, lactose has a
25 marginal, but still detectable effect upon calcium solubility. However, additions of sodium
26 chloride up to 100 g/L result in a much greater increase in calcium solubility. Beyond this
27 point, the concentrations of ions in the solution decreases significantly. These changes in
28 calcium solubility can readily be explained through changes in the activity coefficients. There
29 is little difference in calcium phosphate speciation between 10 and 30°C. However, at 50°C,
30 the ratio of calcium to phosphate in the solution is lower than at the other temperatures and
31 varies less with ionic strength. While the addition of sodium lactate has less effect upon
32 calcium solubility than sodium citrate, it still has a greater effect than sodium chloride at an
33 equivalent ionic strength. Conversely, when these organic anions are present in the solution
34 in the acid form, the effect of pH dominates and results in much higher solubility and a
35 calcium/phosphate ratio close to one, indicative of dicalcium phosphate dihydrate as the
36 dominant solid phase.

37

38 1. INTRODUCTION

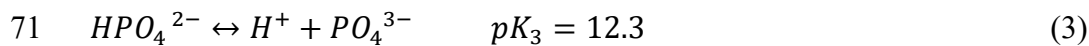
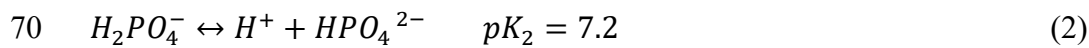
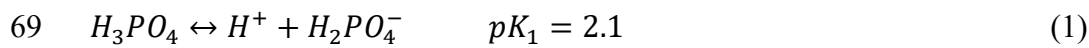
39 With increasingly stringent environmental regulation, dairy industries in Australia are under
40 pressure to pretreat saline effluent so as to improve the quality and reduce the volume of
41 discharged effluent. This effluent stream comprises small amounts of milk sugar, large
42 concentrations of sodium chloride (NaCl) from cheese manufacturing plants, as well as
43 smaller amounts of divalent salts such as calcium phosphates. Due to the low economic value
44 of the discharged effluent, any concentration process should be performed at minimum cost.
45 Such processes are commonly conducted by membrane filtration or thermal evaporation.
46 During the concentration process, heterogenous precipitation of minerals on the surface of
47 evaporators or membrane modules often occurs, creating a major fouling issue and reducing
48 the lifetime of the equipment. If the salt concentration exceeds the limits set by local water
49 authorities, it may then be necessary to divert the saline effluent to a brine pond, where
50 further precipitation occurs.

51 The primary precipitating agent is calcium phosphate, which possesses low solubility in
52 comparison to sodium chloride or lactose. Studies of the solubility of calcium phosphate are
53 complex and ongoing, due to incongruent dissolution phenomenon and dynamic intermediate
54 equilibria¹⁻⁴. Calcium phosphate is a biomineral, which can exhibit various forms with
55 different ratios of calcium to phosphate. The solubility of calcium phosphate is also affected
56 by pH, temperature, the presence of ionic impurities and their concentration, the total ionic
57 strength and the precipitation rate^{5, 6}. Compared to the other parameters, pH has the most
58 profound effect and has been extensively studied⁷⁻⁹.

59 The solubility of different calcium phosphate compounds across variable pH ranges are listed
60 in Table 1. In cheese whey where the pH is typically 4 – 5, dicalcium phosphate dihydrate
61 (DCPD) is the most common precipitant. At higher pH, salts such as octacalcium phosphate

62 (OCP) or hydroxyapatite (HAP) are more thermodynamically stable (Table 1). However in
63 dairy processing, DCPD often remains dominant. This is usually attributed to faster
64 crystallization kinetics for DCPD^{10, 11, 12}. Inhibition of HAP and subsequent formation of
65 DCPD has also been attributed to the presence of citrates in these dairy systems^{13, 14}.

66 At room temperature, phosphoric acid dissociates based on the pH of the environment, as
67 shown below¹⁵. This ionization governs the cation pairing mechanism to maintain electro-
68 neutrality within the solution.



72 In dairy systems such as saline effluent and salty whey permeate, the solubility is also greatly
73 affected by the presence of background electrolytes. In particular, high concentrations of
74 NaCl and organic anions such as lactate and citrate are often present. For example, in a saline
75 effluent such as salty whey permeate, the concentration of citrate ranges from 0.8 mM to 3.6
76 mM. Citrate is known to sequester calcium to form the soluble calcium citrate anion (CaCit⁻),
77 which increases calcium solubility^{16, 17}. In fresh salty whey permeate, lactate concentration
78 can vary from 1.6 mM to 37 mM. This lactate concentration can further increase with time
79 due to the action of residual lactic acid bacteria which convert lactose into this acid. Indeed,
80 we have observed lactate concentrations of over 100 mM for samples stored in our laboratory
81 for six months.

82 The initial amount of NaCl can range between 30 g/L to 100 g/L (0.5 – 1.7M) and this could
83 be concentrated up to an equivalent of 250-300 g/L (> 4 - 5.1M) during effluent treatment.
84 Similarly, the calcium concentration might start at 40mM (7 g/L DCPD) but increase to 120

85 mM (20 g/L DCPD) during concentration¹⁸. Further, process temperatures can swing between
86 production and effluent treatment steps, ranging from 4°C to greater than 50°C. There is
87 currently little information regarding the solubility and precipitation behavior of calcium
88 phosphate under such operating conditions.

89 The current study aims to deepen our understanding of these processes and to assess the
90 possibility for selective precipitation of calcium phosphate salt. To achieve this objective, we
91 mimic the impurities and ionic strength of saline effluent in a full-scale system.
92 Understanding the precipitation of calcium phosphate in the presence of extreme
93 concentrations of NaCl and organic anions and acids will aid in mitigating mineral scaling
94 and thus prolong the lifetime of equipment through the adjustment of operating conditions.
95 These findings have applications beyond the treatment of dairy saline effluent, encompassing
96 water treatment processes within other chemical industries.

97

98 2. MATERIAL AND METHODS

99 **Materials**

100 All chemicals used were analytical grade and were used as received without further
101 purification. For experiments and cleaning procedures, purified water (Elix Millipore,
102 resistivity $> 15 \text{ M}\Omega \text{ cm}^{-1}$) was used. For analytical procedures and preparation of standard
103 solutions, water of higher purity (Milli-Q Millipore, resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$) was used.

104 Dicalcium phosphate dihydrate, DCPD ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $>98\%$) was obtained from Astral
105 Scientific. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $>99\%$), di-Sodium hydrogen phosphate
106 (Na_2HPO_4 , $>99\%$) and lactose monohydrate ($\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$) were purchased from Chem
107 Supply. To adjust the pH and organic anion concentration, tri-sodium citrate (Na_3Cit , $>99\%$),
108 sodium lactate ($\text{NaC}_3\text{H}_5\text{O}_3$, $>70\%$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, $>99\%$) and lactic acid ($\text{C}_3\text{H}_6\text{O}_3$,
109 85%) were purchased from Chem Supply and nitric acid (HNO_3 , 69.5%) was purchased from
110 Scharlau.

111 **Methods**

112 The experiments were performed using an end-point equilibrium technique. This technique
113 operates by incubating excess amounts of solid in a pre-conditioned background solution at
114 constant temperature. It has been widely utilized for solubility measurement¹⁹. In the present
115 case, a consistent excess amount (2 g unless otherwise stated) of solid DCPD ($\text{Ca/P} = 1$) was
116 added to 200 ml of a background solution in a glass container, as shown in Figure 1. The
117 composition of the background solution was adjusted to be between 0 – 300 g/L (5.1 M)
118 NaCl and 0 to 100 g/L (0.3M) of lactose. The role of organic acid and anions was determined
119 using a background solution of 1 to 100 mM of either lactic or citric acid, sodium lactate or
120 sodium citrate. The vessel was double-sealed using Parafilm M,R Laboratory film (SPI

121 supplies) and capped to avoid evaporation. It was then incubated in a circulating water bath
122 (Julabo) controlled at 10°C, 30°C or 50°C for 168 hours (one week). A constant stirring rate
123 was set at approximately 250 rpm. At the end of the incubation period, the supernatant was
124 filtered using a 0.2 µm (polyethersulfone, PES) syringe filter (Millipore) and the composition
125 of the supernatant liquor was analysed. The pH was measured at the beginning and at the end
126 of the experiment, using a WP81 double junction glass pH electrode and temperature probe,
127 connected to a digital benchtop meter. Each experiment was carried out at least in duplicate.

128 At the conclusion of experiments, the concentration of Ca, Na and phosphorus (P) was
129 measured using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)
130 (Varian 720-OES). The concentrations of the orthophosphate anions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-})
131 and chloride (Cl^-) were determined using Ion Chromatography (Dionex 1000CS) with an AS
132 14 anion exchange column. The concentration of lactate and citrate was quantified using
133 Reverse Phase High Performance Liquid Chromatography (RP-HPLC) (Shimadzu LC-20AT)
134 employing an ion-exchange column (HPX-87H). Triplicate measurements were performed
135 for each independent sample and the error margins are based on a single standard deviation of
136 these results (n=6). Data was analysed using one way analysis of variance (ANOVA), with a
137 significance level of $p = 0.01$.

138 The behavior of calcium and phosphate ions in the solution was also simulated through
139 predictions of the activity coefficient of these ions at ionic strengths of 0 to 5M NaCl.
140 ASPEN Plus V8.6 (Aspen One) was employed using the Pitzer thermodynamic package.

141

142 3. RESULTS AND DISCUSSION

143 **Effect of neutral solute (lactose)**

144 It was expected that lactose would not alter the solubility of calcium phosphate, as a neutral
145 solute should not dictate ion speciation phenomena. However, there was a significant increase
146 ($p < 0.01$) in the concentration of soluble calcium from 0.68 ± 0.06 mM to 1.33 ± 0.10 mM,
147 as the lactose concentration increased from 0 to 100 g/L (Figure 2). It can also be seen from
148 Figure 2b that the calcium to phosphate ratio (Ca/P) in the supernatant in the absence of
149 lactose or NaCl is significantly less than unity ($p < 0.01$), indicating that the solid phase has a
150 Ca/P ratio greater than unity, indicative of significant quantities of HAP or OCP (Table 1).
151 As the amount of the remaining excess solid in the solution is significantly greater than the
152 amount dissolved, an accurate mass balance of the solid could not be conducted to confirm
153 the exact solid phase composition.

154 Increasing the lactose concentration significantly increases ($p < 0.01$) the Ca/P ratio, from
155 0.54 ± 0.01 to 0.70 ± 0.01 mM. The effect of sugars on different calcium salts has also been
156 observed by Doherty et al.²⁰ in a calcium oxalate-sucrose system. Besic²¹ claims that
157 sucrose in food products affects the solubility of calcium and phosphate in teeth. Other
158 workers have shown that calcium salts can significantly influence the solubility and growth
159 rate of lactose crystals due to the formation of a lactose complex^{22, 23}. The changing
160 solubility may also reflect a decrease in the water activity as the lactose concentration
161 increased, consistent with the observation of a very small conductivity increase. However,
162 while lactose clearly impacts calcium solubility, the effect is very small, when compared with
163 NaCl, as also seen in Figure 2(a). The remainder of this work therefore focuses on the impact
164 of such ionic species.

165

166 **Effect of ionic strength**

167 It can be seen from Figure 3 that the concentration of the calcium ion in the supernatant
168 increases significantly for all temperatures as the NaCl concentration increases to 100g/L.
169 Beyond this point, a significant ($p < 0.01$) decrease in both the soluble calcium and phosphate
170 concentration is observed. This decreased solubility of calcium in solution at the highest
171 NaCl concentrations is of significance in understanding fouling in equipment such as brine
172 evaporators, which may operate under such conditions. The decreased solubility could cause
173 rapid calcium scaling to occur.

174 These trends in solubility can be understood by reference to the activity coefficient of the
175 ions in solution. With increasing ionic strength, the activity coefficient of both calcium and
176 phosphate ions decrease (Figure 4) resulting in increased solubility. This loss in activity
177 results from ion-pairing (association), which has been previously investigated²⁴⁻²⁶, up to the
178 ionic strength of seawater (approximately 35 g/L or 0.7M) at room temperature. Millero et
179 al²⁶ uses the Pitzer equation to predict that the activity coefficient of Ca^{2+} should decrease
180 from 0.851 at an ionic strength of 0.002 M down to 0.225 at an ionic strength of 0.7 M at 25
181 °C. Their study also predicts that the activity coefficients for H_2PO_4^- decrease from 0.947 to
182 0.363 and for HPO_4^{2-} from 0.758 to 0.044. Comparable values were generated in the present
183 case, as shown in Figure 4. However, beyond a salt concentration of 100 g/L the activity
184 coefficients for calcium increase again.

185 Prediction of the supernatant concentration using these activity coefficients is a complex
186 problem given the solid phase equilibria between OCP, HAP and DCPD, in addition to the
187 phosphate speciation given by Equations 1 to 3. Figure 5 shows a simulation for the simplest
188 case where DPCD is assumed to be the only solid phase, using the solubility constant
189 provided in Table 1 at 25°C. It is clear that even this simple simulation provides a reasonable

190 fit to the supernatant calcium concentration. The phosphate concentrations are higher, again
191 suggesting that the solid phase contains OCP or HAP in addition to DCPD.

192 With increasing ionic strength a small decrease in pH was observed. The pH fell from 7.67
193 ± 0.25 in the absence of NaCl to 7.00 ± 0.22 at 300 g/L NaCl. At comparable pH values and
194 at zero NaCl concentration, the Ca/P ratio observed (Table 2) is similar to the value reported
195 by Sutter et al. from their leaching experiments ²⁷. However, with increasing ionic strength,
196 the Ca/P ratio increases significantly at both 10 °C and 30 °C, with values in the range of
197 0.72-0.77 at 10 to 300 g/L NaCl. This suggests a shift back from OCP or HAP towards
198 DCPD, consistent with the common observations in dairy processing. Conversely, there is no
199 significant shift in the Ca/P ratio at 50°C, implying that at this temperature, the crystal
200 morphology is unaffected by ionic strength. Figure 4(b) also shows that the ionic strength
201 affects the activity of H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} to differing extents, which alters the
202 equilibria of these species. These changes may also explain the observed pH variation.

203
204 Some workers have argued that the amount of excess solid existing in the system alters the
205 solubility of calcium phosphate, with the lowest solubility occurring for the smallest amount
206 of solid ^{1, 28, 29}. This is consistent with the present results shown in Figure 6. In the absence of
207 NaCl, no significant difference could be observed ($p < 0.01$), as the amount of $[\text{Ca}^{2+}]$
208 dissolved in the solution is very low. However, at higher ionic strength, it can be seen that the
209 solubility is significantly affected ($p < 0.01$) by the amount of remaining excess solid in the
210 solution. These differences have been reported to relate to the different calcium phosphate
211 polymorphs that can form and the resulting equilibria between multiple solid phases, in
212 addition to the liquid-solid phase equilibria. These authors argue that this is the reason that
213 the solubility data reported by researchers using different techniques often shows wide
214 variability.

215

216 **Effect of Temperature**

217 The solubility of both calcium and phosphate is identical within experimental error at 10 °C
218 to 30 °C for NaCl concentrations of up to 50 g/L (Figure 3). However, beyond this
219 concentration, the solubility at 30°C is significantly lower than that at 10°C ($p < 0.01$).
220 Changes in solubility with temperature are more apparent at 50°C, with the solubility
221 increasing significantly ($p < 0.01$) at all NaCl concentrations. Sutter et al.²⁷ observed a slight
222 decrease in the concentration of soluble calcium in the solution from temperatures of 5 °C to
223 37 °C using a leaching technique (at comparable pH ~ 6.5-6.8) and from 25°C to 37°C in
224 batch experiments at near neutral and acidic conditions. On the other hand, Green and Perry
225³⁰ report an increasing solubility of monobasic calcium phosphate with respect to
226 temperature. These literature results are all broadly consistent with the work presented here.
227 However, the temperature effects in this case should not be oversimplified as the Ca/P ratio in
228 the solution is also significantly altered, especially at 50 °C where this ratio decreases to 0.45
229 ± 0.05 (Table 2).

230 The results appear initially inconsistent with many previous studies, which claim that calcium
231 phosphate solubility declines with temperature³¹⁻³³. Indeed, in our own work, we have also
232 previously observed that increasing the temperature could shorten the time it takes for the
233 first appearance of crystals in saline dairy effluent³⁴. However, these references generally
234 describe kinetic effects, where increasing temperature causes calcium salts to precipitate in a
235 shorter time. The present work and that of the literature cited above considers the final
236 equilibrium after at least 168 hours, where such kinetic effects become irrelevant.

237

238

239 **Effect of Organic anions**

240 Figure 6 shows the concentration of calcium in the solution in the presence of either the
241 organic lactic and citric acids, or the strong acid HNO₃. The increasing solubility of calcium
242 phosphate with respect to pH is well known (pH < 6), although this effect varies depending
243 upon the pKa of the specific acid. The role of pH in governing the solubility of calcium
244 phosphate salts by addition of orthophosphoric acid has been reported^{35, 36}. However,
245 orthophosphoric acid exhibits both weak acid and polybasic properties, and will alter the
246 amount of available phosphate in the solution through the common ion effect. In this study,
247 HNO₃ is used to isolate the role of pH, as the formation of Ca(NO₃)₂ is unlikely to occur.

248 In 1 mM HNO₃, lactic acid or citric acid, the initial pH of the solution (with 20 g/L DCPD)
249 is 4.61 ± 0.14 , 5.67 ± 0.38 and 5.00 ± 0.33 , respectively. Within this pH range the
250 concentration of calcium recorded in solution is comparable to the value reported by Sutter et
251 al.²⁷ obtained using a leaching method where the pH was adjusted using H₃PO₄. The values
252 recorded at 1 mM are also comparable with that obtained by other workers using OCP as the
253 starting solid³⁷. The calcium solubility is lowest for the lactic acid (p<0.01), reflecting its
254 weak acidity and hence the relatively high pH of the solution. The solubility of the nitric and
255 citric acids are comparable within experimental error, even though the pH of the citric
256 solution is higher than that of the nitric. This reflects the calcium sequestering capacity of the
257 citrate anion.

258 Discrepancies with the literature are observed at higher acidity (10 mM, see Figure 7). The
259 solubility of calcium in the solution is two to four times lower compared to the concentration
260 reported by Sutter et al.²⁷. At the end of experiments, these workers obtain a value of 47mM
261 at similar pH (pH 2.90 and 3.53 for HNO₃ and lactic acid respectively in this work, versus

262 3.38 in the Sutter et al. study). This might be due to the utilisation of different acids here
263 instead of orthophosphoric acid.

264 Figure 8a shows that the solubility of calcium ions increases significantly ($p < 0.01$) as the
265 sodium lactate concentration increases from 1 to 100 mM at 10 and 30 °C. The use of sodium
266 lactate in these experiments ensures that the pH of the solution changes little, within the range
267 of pH 7.0 to 8.7. The increased solubility is partly associated with the increase in the
268 background ionic strength. Nevertheless, the effect of sodium lactate on the solubility of
269 calcium and phosphate is more pronounced than NaCl at an equivalent concentration.
270 Specifically, the effect of 100 mM sodium lactate on calcium solubility is equivalent ($p > 0.05$)
271 to 170 mM (10g/L) of NaCl at 10 °C and 30 °C (see Table 3).

272 At 50°C, the pH falls significantly upon addition of sodium lactate, suggesting that
273 different calcium phosphate speciation is occurring. The calcium solubility increases further,
274 but it is difficult to confirm whether this is due to the lactate or the shift in pH.

275 In dairy effluent, the amount of citrate is relatively low compared to lactate. However,
276 much greater increases in the concentration of calcium in the solution are observed when the
277 citrate anion is added to solution (Figure 8a). The contribution of pH is again minimized here
278 through utilization of tri-sodium citrate (pH 7.3-8.2). It is clear that citrate shows a strong
279 calcium sequestering capacity, as has been widely reported elsewhere^{4, 35, 38-43}. The effect of
280 temperature on the saturation concentration of calcium in the presence of the citrate anion is
281 less clear than with lactate or chloride, due to the dominant effect of citrate sequestration
282 (Figure 8a).

283 A steady increase in the calcium concentration in the solution is observed for both organic
284 acids as shown in Figure 8b. The sequestering capacity of citrate dominates over the
285 contribution of pH under all conditions, with the total calcium in the citric acid solution three

286 to four times higher than in lactic acid. Further, analysis indicated that after 168 hours
287 equilibration, from an initial concentration of 10 mM of organic acid, 5.4 ± 0.8 mM of citrate
288 was consumed whereas only 1.5 ± 0.3 mM lactate was consumed for the same amount of
289 DCPD. At 100mM (Figure 6), the concentration of calcium in the solution is largely the
290 same for lactic and nitric acid, which confirms that the increase in solubility for lactic acid is
291 solely due to phosphate dissociation at these extreme pH levels (DCPD in 100mM HNO₃ pH
292 1.75 and in 100 mM lactic acid pH 2.68).

293 The addition of sodium lactate has minimal impact on the Ca/P ratio at 30°C (see Figure 9).
294 Conversely, the addition of trisodium citrate increases the amount of the available calcium in
295 the solution due either to formation of CaCit⁻ or to the preferential formation of DCPD^{13, 14}.
296 The addition of lactic acid causes the Ca/P ratio to increase to unity. This is consistent with
297 the literature; DCPD is the most stable salt at pH less than 5.5 (Table 1). A similar increase
298 was expected for citric acid, however this was not clearly observed, with the Ca/P in this case
299 showing significant variability (data not shown).

300 As with the systems containing NaCl (Table 2) in systems at neutral pH, high temperature
301 (50 °C) results in a lower Ca/P ratio in solution ($p < 0.01$) implying preferential formation of
302 HAP or OCP (Table 4). In the presence of lactic acid, the Ca/P ratio remains close to unity
303 regardless of the temperature. This shows the dominating effect of pH in comparison to other
304 parameters. Conversely, with citric acid, this ratio falls with temperature ($p < 0.01$).

305

306 **Effect of high ionic strength in the presence of lactic acid**

307 In real saline waste effluent, the background electrolyte comprises a mixture of ions. Figure
308 10 shows the saturation concentration of calcium in a mixture of NaCl with 10 mM of lactic

309 acid at 30 °C. The pH range throughout the whole experiment was 3.7 ± 0.6 . It can be seen
310 that the trends in solubility observed with NaCl alone (Figure 3) are no longer observed.
311 Instead, the concentration of calcium in the solution remains relatively constant at the same
312 value as for 10mM lactic acid alone (7 mM). This again reflects the stronger influence of pH,
313 relative to those of ionic strength alone.

314 Despite the dominance of pH in determining the calcium solubility, the presence of NaCl
315 still significantly affects the Ca/P ratio. In the absence of NaCl, the Ca/P ratio observed is
316 1.01 ± 0.03 which is consistent with the Ca/P ratio across a broad range of acidic conditions.
317 However, in the presence of NaCl the Ca/P ratio falls significantly ($p < 0.01$) to 0.8 ± 0.03 .

318 4. DISCUSSION

319 In this work, the solubility of calcium phosphate in the presence of high concentrations of
320 lactose, sodium chloride, lactate and citrate and under conditions of variable acidity and
321 temperature has been investigated. Lactose has a marginal but significant effect upon the
322 saturation concentration of calcium in the solution, possibly due to the formation of a
323 complex of lactose with calcium salts. Increasing ionic strength through the addition of NaCl
324 up to 100 g/L within the temperature range of 10°C to 50°C, reduces the activity of Ca^{2+}
325 resulting in an increase of calcium in the solution. Above this NaCl concentration, the
326 calcium solubility declines, particularly at 50°C. This latter finding is of importance in
327 understanding calcium scaling in high salt solutions. The addition of salts such as sodium
328 chloride or trisodium lactate has differing effects on the solubility of H_2PO_4^- and HPO_4^{2-} at
329 different temperatures, so that at 10 and 30°C, the Ca/P ratio increases from around 0.5 to
330 0.7-0.8, while at 50°C this ratio remains low.

331 The lactate anion shows only a very small calcium sequestering capacity compared to the
332 citrate anion, but is still a more effective sequestering agent than chloride. Specifically, at

333 10°C and 30°C, the same calcium solubility is achieved by 100 mM sodium lactate as 170
334 mM sodium chloride. However, when lactate is added as an organic acid, the role of pH
335 dominates, providing large increases in the calcium concentration and resulting in the Ca/P
336 ratio reaching unity.

337 In a real effluent solution comprising an abundant amount of both NaCl and lactic acid, the
338 effect of pH dominates the saturation concentration of calcium, but crystal morphology is still
339 affected by the NaCl concentration, as indicated by changes in the Ca/P ratio.

340 Lastly, experiments showed some evidence in support of previous work by other authors
341 that have suggested that calcium solubility can be affected by the quantity of excess solid in
342 the solution.

343 344 5. ACKNOWLEDGMENTS

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- 453

454 TABLE CAPTIONS

455 Table 1. The various forms of calcium phosphate that can form in aqueous solution and their
456 solubility at 25°C and neutral pH⁵.

457 Table 2. The Ca/P ratio in the supernatant after 168 hours equilibration of 10 g/L DCPD, with
458 a background concentration of NaCl. Superscripts indicate samples that are not significantly
459 different ($p > 0.01$).

460 Table 3. The Calcium and phosphorus concentrations in the supernatant after 168 hours
461 equilibration of 10 g/L DCPD, with a background concentration of NaCl or sodium lactate.
462 Superscripts indicate samples that are not significantly different ($p > 0.01$).

463 Table 4. The Ca/P ratio in the supernatant after 168 hours equilibration of 10g/L DCPD, with
464 a background concentration of organic anions. Superscripts indicate samples that are not
465 significantly different ($p > 0.01$).

466

467

468 FIGURE CAPTIONS

469 Figure 1. Schematic diagram of the end-point equilibrium technique.

470 Figure 2. (a) The concentration of calcium and (b) the calcium to phosphate ratio in the
471 supernatant after 168 hours of equilibration at 30°C of 10 g/L DCPD, with a background
472 concentration of NaCl or lactose.

473 Figure 3. The concentration of calcium in the supernatant after 168 hours of equilibration
474 of 10 g/L DCPD, with a background concentration of NaCl.

475 Figure 4. (a) Activity coefficient of Ca^{2+} (b) Activity coefficient of orthophosphates
476 simulated using the Pitzer model within ASPEN Plus V8.6 at 25°C. Concentrations of
477 calcium, phosphate and hydronium simulated were 10mM.

478 Figure 5. Comparison of the experimental data for calcium and phosphorus concentrations
479 in the supernatant at 30°C with a simulation that assumes that DCPD is the only salt ($\text{Ca/P} =$
480 1) and uses the activity coefficients determined from the Pitzer model and the solubility
481 constant from Table 1 at 25°C.

482 Figure 6. Concentration of Ca^{2+} in the supernatant after 168 hours equilibration of 10g/L
483 DCPD and 1.25g/L DCPD at 30°C.

484 Figure 7. Concentration of calcium in the supernatant after 168 hours of equilibration of
485 20g/L DCPD at 30°C, with a background acid concentration (a) absolute concentrations (b)
486 concentrations relative to the nitric acid case.

487 Figure 8. (a) The concentration of Ca^{2+} in the supernatant with a background concentration
488 of an organic anion i.e. sodium lactate and trisodium citrate (pH 7.0-8.7) (b) The
489 concentration of Ca^{2+} in the supernatant with a background concentration of organic acid i.e.

490 lactic acid and citric acid (pH 2.68 - 6.00) after 168 hours of equilibration of 10g/L DCPD.

491 The NaCl concentration is zero. Note the different x-axis scales on the two graphs.

492 Figure 9. The calcium to phosphate ratio in the supernatant after 168 hours of equilibration

493 at 30°C of 10 g/L DCPD, with a background concentration of lactic acid, trisodium citrate or

494 sodium lactate.

495 Figure 10. Concentration of calcium and phosphorous in the supernatant after 168 hours of

496 equilibration at 30°C of 10g/L in 10 mM lactic acid, with a background concentration of

497 NaCl.

498

499 Table 1

Ca/P mol ratio	Compound	Formula	Solubility 25°C -log (Ksp)	pH* 25°C
0.5	Monocalcium phosphate monohydrate (MCPM)	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	1.14	0.0-2.0
1.0	Dicalcium phosphate dihydrate (DCPD, brushite)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	6.59	2.0-6.0
1.3	Octacalcium phosphate (OCP)	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	96.6	5.5-7.0
1.2-2.2	Amorphous calcium phosphates (ACP)	$\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$ $n=3-4.5$	***	5.0-12.0
1.5-1.7	Calcium deficient hydroxyapatite (CDHA)	$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ($0 < x < 1$)	≈ 85	6.5-9.5
1.7	Hydroxyapatite (HAP)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	116.8	9.5-12.0

500 *pH where the solid can exist in aqueous solution at room temperature.

501 ***cannot be precisely measured, in acidic buffer $\text{ACP} < \text{CDHA} < \text{HAP}$.

502

503 Table 2

	0 g/L NaCl	10 g/L NaCl	100 g/L NaCl	300 g/L NaCl
10°C	0.52 ± 0.06 ^a	0.74 ± 0.04 ^b	0.74 ± 0.03 ^b	0.77 ± 0.01 ^b
30°C	0.54 ± 0.03 ^a	0.72 ± 0.01 ^b	0.77 ± 0.02 ^b	0.72 ± 0.04 ^b
50°C	0.45 ± 0.03 ^c	0.46 ± 0.01 ^c	0.44 ± 0.02 ^c	0.46 ± 0.04 ^c

504

505

506 Table 3

	Calcium (mM)		Phosphorus (mM)	
	170 mM NaCl	100 mM NaLactate	170 mM NaCl	100 mM NaLactate
10°C	1.97 ± 0.13	1.99 ± 0.22	2.65 ± 0.15	2.46 ± 0.05
30°C	1.96 ± 0.11	1.87 ± 0.10	2.67 ± 0.06	2.71 ± 0.03

507

508

509 Table 4

10°C	30°C	50°C	10°C	30°C	50°C
Sodium Lactate			Trisodium Citrate		
0.66 ± 0.04^a	0.61 ± 0.04 ^a	0.45 ± 0.01 ^b	0.84 ± 0.06 ^c	0.81 ± 0.03 ^c	0.27 ± 0.04 ^d
Lactic Acid			Citric Acid		
0.96 ± 0.08^e	1.04 ± 0.04 ^f	0.92 ± 0.03 ^e	0.88 ± 0.07 ^g	0.78 ± 0.04 ^c	0.64 ± 0.03 ^a

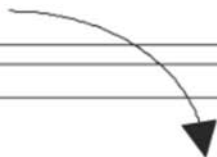
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DCPD

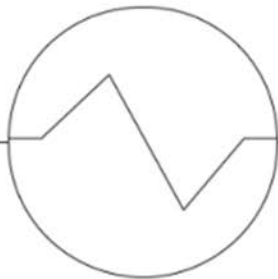


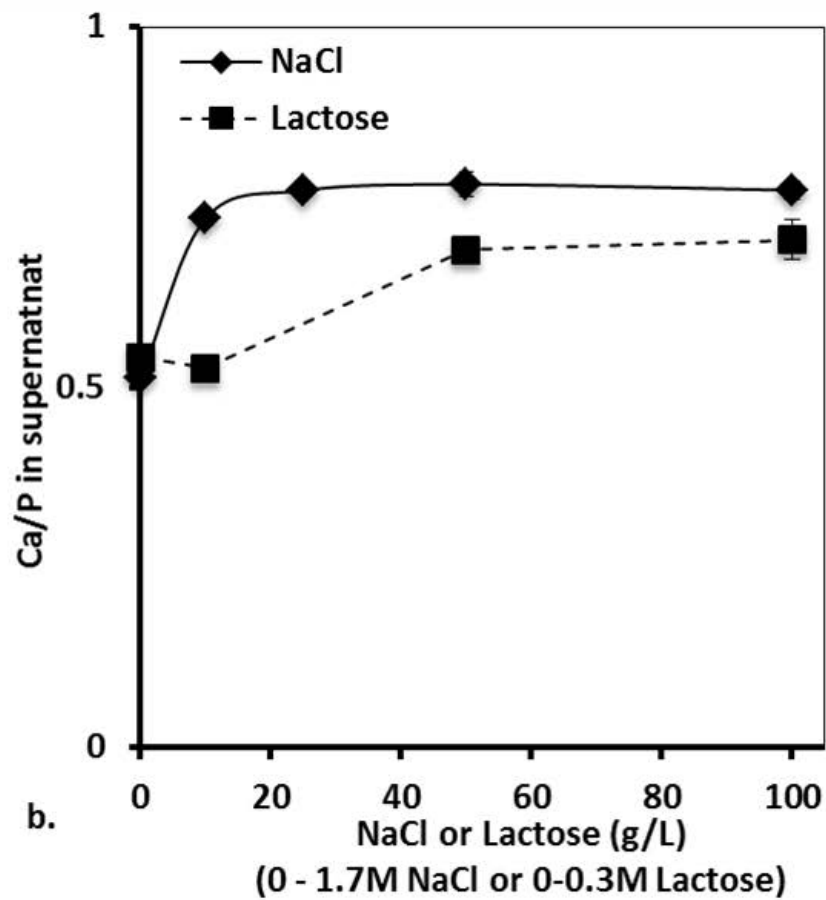
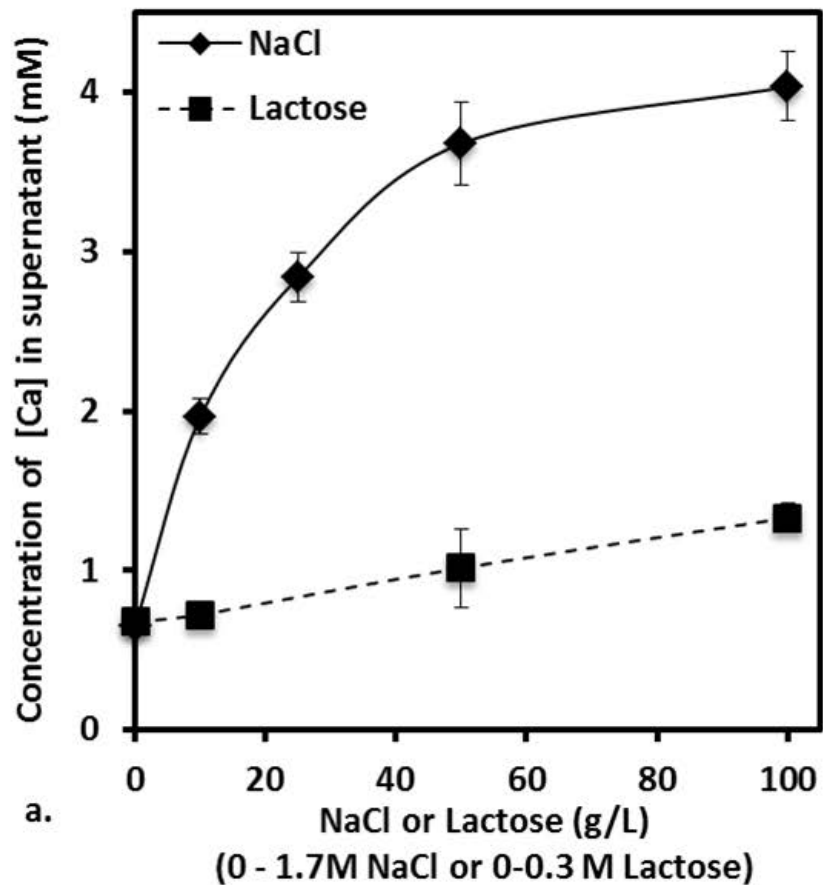
NaCl (0 – 300 g/L)
Lactose (0 – 100 g/L)
Organic anion/acid (0 – 100mM)

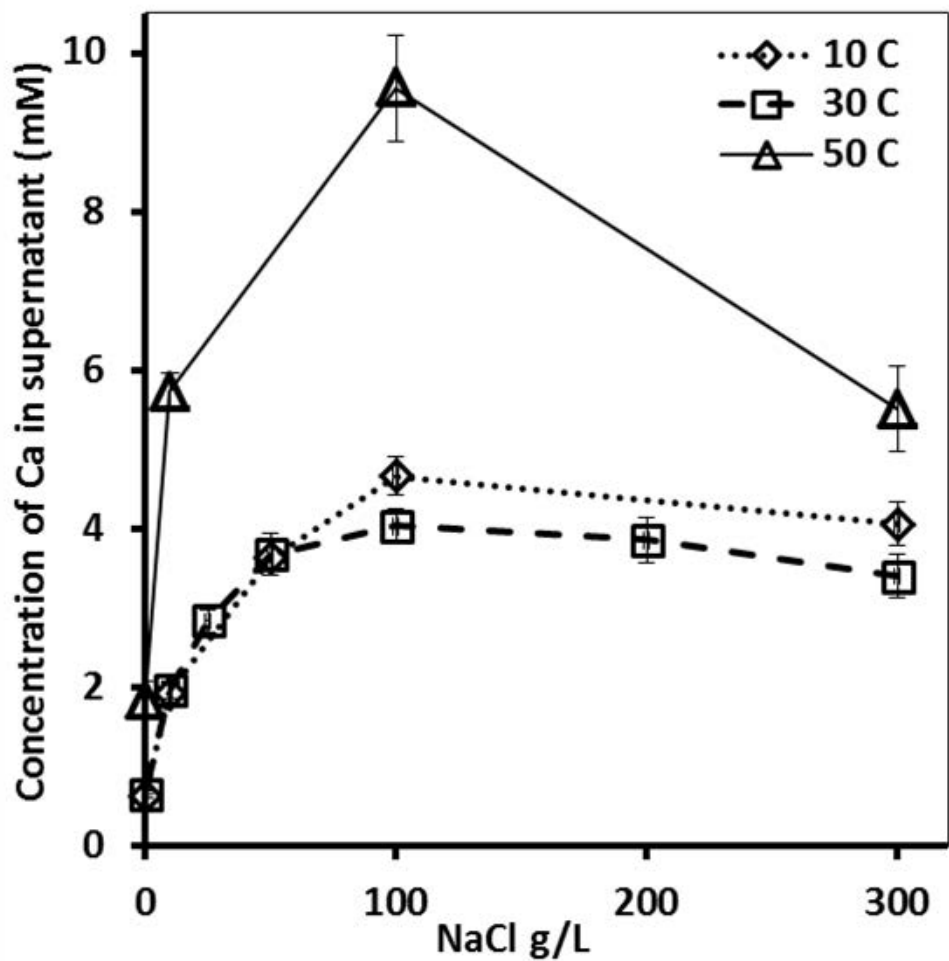


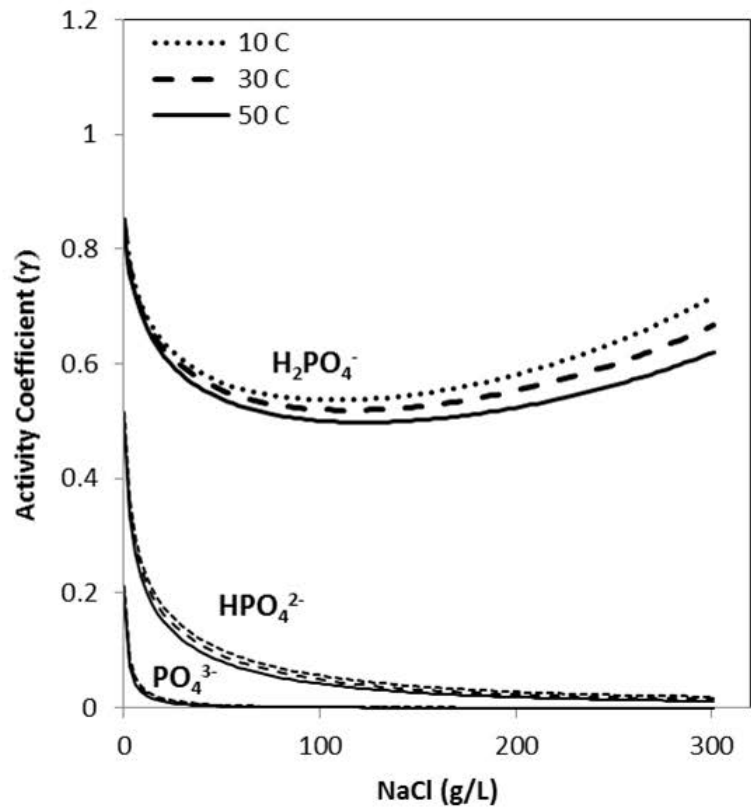
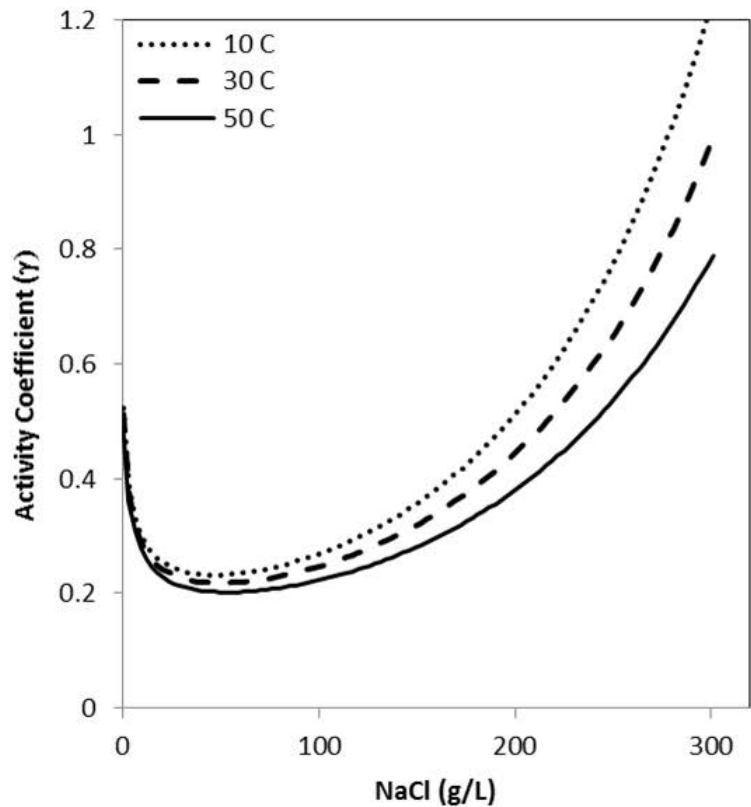
Water Jacket

Stirrer Plate (250 rpm)









Concentration of Ca and P (mM)

