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1 **Calcium citrate insolubilization drives the fouling of falling film evaporators during the**
2 **concentration of hydrochloric acid whey**

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13 Full title: Calcium citrate insolubilization drives the fouling of falling film evaporators during
14 the concentration of hydrochloric acid whey

15 **Abstract**

16 When dairy powders are produced, the mineral fraction undergoes strong modifications
17 during the vacuum concentration step, leading to the fouling of falling film evaporators. The
18 objective of this study was to determine the nature of the deposits formed during the vacuum
19 concentration of two fouling and highly mineralized products: hydrochloric acid whey and
20 lactic acid whey. These products mainly differ in terms of their mineral composition: lactic acid
21 whey contains a high level of lactic acid and traces of citrate, whereas hydrochloric acid whey
22 contains citrate and no lactic acid. Concentrates at different concentration factors were
23 produced using a pilot-scale falling film evaporator. The compositions of the fouling deposits
24 as well as the precipitates present in the concentrates were deduced from the analytical
25 determination of the composition of the concentrates and their respective diffusible phases. The
26 behavior of the mineral fraction of both acid wheys during concentration was shown to be very
27 different. In the case of hydrochloric acid whey, experimental results suggested a deposition of
28 calcium and citrate ions in the evaporator as well as their precipitation in the highly concentrated
29 products. On the contrary, neither mineral deposition nor precipitation occurred during the
30 concentration of lactic acid whey. This study underlined the key role of citrate ions in the
31 fouling of evaporators during the concentration of hydrochloric acid wheys.

32 **Keywords:** vacuum evaporation – acid whey – fouling – calcium citrate – lactic acid – mineral
33 deposit

34

35 **1. Introduction**

36 Whey is a co-product of cheese and casein production. Undervalued in the past, it is now a
37 valuable offshoot of dairy product manufacturing due to the growing demand for whey in infant
38 formula and as a nutrient in dietetic and health foods. Even though there is a wide variability in
39 their compositions depending on the processing conditions (Saulnier et al., 1995), wheys can
40 be further classified into two groups in terms of their acidity. Sweet whey comes from the
41 cheese manufacturing process that uses rennet-type enzymes. Its pH is around 6.4-6.6 and it is
42 composed of water (94% liquid), lactose (75% w/w dry matter content, DM), proteins (13%
43 w/w DM), minerals (8-9 % w/w DM) and fat (1% w/w DM) (Pearce, 1992). Given its high
44 lactose content and protein composition, sweet whey is commonly spray-dried and used in high-
45 value dairy powders such as those used for infant nutrition. Acid wheys result from the
46 production of acid-coagulated dairy products, including fresh cheeses and caseins. They contain
47 more minerals than sweet whey due to the solubilisation of colloidal calcium and inorganic
48 phosphate during milk acidification (Zall, 1992). The high mineralization of acid wheys limits
49 their processing performance as well as their potential uses in human nutrition due to nutritional
50 unbalance (Batchelder, 1987). For example, during the evaporation process, the precipitation
51 and deposit of mineral salts on heating surfaces of falling film evaporators are favored. This
52 deposition of matter on heating surfaces is known as fouling.

53 Fouling is a consequence of the numerous changes that undergo the product components
54 during vacuum evaporation. These changes affect the biochemical, physical and rheological
55 properties of the product itself (Singh & Newstead, 1992; Walstra & Jenness, 1984). Their
56 amplitude are not always proportional to the concentration factor because some effects are
57 offset by others. As an example, the activity of the solutes increases due to the concentration
58 but is not directly proportional to the concentration factor since the increasing ionic strength

59 decreases the activity coefficients. In turn, the reduced activity coefficients lead to an increase
60 in the ionization and solubility of salts (Walstra & Jenness, 1984).

61 Concentration has an impact on salt equilibrium since solubility products may be exceeded and
62 salts may then precipitate with increasing concentration factors, as is the case for calcium
63 phosphate and calcium citrate (Walstra & Jenness, 1984). This precipitation, combined with an
64 increased ionization of ionic species and the concentration of H^+ ions, induces a decrease in the
65 pH of the solution and an increase in the ratio of monovalent to divalent cations. Concerning
66 proteins, lowering the pH and increasing ionic strength favors their association since it comes
67 with closer packing of molecules, decreasing thickness of the ionic double layer and lower
68 apparent isoelectric pH (Walstra & Jenness, 1984).

69 Concentration also affects the physical properties (density, refractive index, heat conductivity,
70 etc.) and the rheological properties of concentrates. They become more and more viscous and
71 clearly exhibit their non-Newtonian behavior beyond a given DM content (Velez-Ruiz &
72 Barbosa-Canovas, 1997). Viscosity is a key parameter in the operation of falling film
73 evaporators since it determines the maximum achievable DM content in this equipment (Gray,
74 1981). Finally, the changes during vacuum evaporation depend to some extent on other
75 parameters such as heat treatment before concentration, operating temperature and residence
76 time in the falling film evaporator or storage time after concentration (Singh & Newstead,
77 1992).

78 Fouling during milk and whey processing is a major problem in the dairy industry and has
79 negative impacts on product quality and operating costs. The undesirable effects of fouling
80 deposits include decreased heat transfer coefficients, reduced process efficiency and product
81 losses, as well as increased cleaning costs and environmental impact (Daufin & Labbé, 1998;
82 de Jong, 1997). Fouling particularly affects the operation of heat exchangers, falling film
83 evaporators and membrane units. Fouling of heat exchangers has been extensively studied and

84 remains a relevant research focus, underlining the complexity of the phenomena involved.
85 Numerous studies and reviews in the literature deal with the nature and mechanisms of
86 deposition and cleaning procedures (Bansal & Chen, 2006; Changani, Belmar-Beiny, & Fryer,
87 1997; Jun & Puri, 2005; Sadeghinezhad et al., 2013; Visser & Jeurink, 1997). On the contrary,
88 few studies have focused on the fouling of falling evaporators. However, it is unlikely that the
89 natures of deposits are similar in falling film evaporators and in heat exchangers (Jeurink &
90 Brinkman, 1994; Morison, 2015). The use of vacuum, the increasing concentration of
91 compounds, the decreasing temperature in the evaporator and the longer residence times make
92 the operating conditions different from those encountered in heat exchangers. As an example,
93 Jeurink & Brinkman (1994) observed the presence of protein deposits in falling film
94 evaporators during the concentration of milk although the proteins had been previously
95 denatured in the preheating section. The authors suggested that due to the concentration of dairy
96 components, reactions other than protein denaturation could be involved in the formation of the
97 fouling deposit. In the same study, the authors provided experimental data about the
98 composition of the deposits formed in industrial falling film evaporators and heat exchangers
99 that differ in composition according to the type of equipment and the product processed.
100 Moreover, after the concentration of whey from 5 to 28% w/w DM, the main components of
101 the deposit were proteins and calcium phosphate, whereas after the concentration of whey from
102 28 to 55% w/w DM, a larger deposit was produced and the main component was calcium citrate.
103 Vavrusova et al. (2017) analyzed the composition of a deposit formed during the concentration
104 of whey permeate using infrared spectroscopy and found that the main component was calcium
105 citrate tetrahydrate. In the meantime, Kessler (1986) found that the main component of deposits
106 was proteins during vacuum concentration of acid whey using a pilot-scale falling film
107 evaporator.

108 In the few studies dealing with fouling in falling film evaporators, deposits came from
109 industrial equipment where operating conditions were not fully controlled. In view of defining
110 appropriate operating conditions, as well as selecting efficient cleaning strategies, a better
111 understanding of the formation and composition of deposits is needed, requiring experimental
112 work at lab- and pilot-scale. The objective of this study was thus to determine the nature of the
113 deposit formed during the concentration of two types of acid whey using a pilot-scale falling-
114 film evaporator. Concentrates of hydrochloric acid whey (HAW) and lactic acid whey (LAW)
115 at different concentration factors were produced under controlled process conditions, making it
116 possible to deduce the nature of the deposit formed on the heating surfaces during the process.
117 Experimental results for both acid wheys were then compared and discussed by taking their
118 differences in composition into account, i.e., the presence of lactate in LAW and citrate in
119 HAW.

120 **2. Materials and Methods**

121 *2.1 Initial raw materials*

122 Fresh acid wheys were provided by local dairy companies. HAW came from a casein factory
123 that uses hydrochloric acid for casein precipitation, whereas LAW was a by-product of fresh
124 cheese production. Their average compositions are given in Table 1. Relative mean
125 uncertainties for the concentration of each acid whey component were below 10% except for
126 lactate and ash contents in initial LAW.

127 *2.2 Concentration of both acid wheys at the pilot scale*

128 Both acid wheys were concentrated in a pilot-scale falling film evaporator (GEA Process
129 Engineering, St Quentin-en-Yvelines, France) composed of three evaporation tubes in series
130 (Fig. 1). The evaporator was well-characterized by Silveira et al. (2013) and Silveira et al.
131 (2015). Its configuration was close to those used in the dairy industry, especially from a
132 hydrodynamic point of view. The tubes were 4-m high and had internal diameters of 0.036 m

133 (first tube) and 0.023 m (second and third tubes). A single porthole on the side of the tubes
134 made it possible to inspect the appearance of their inner surfaces. Each of the tubes was
135 equipped with an electric boiler that provided energy for water evaporation. The three tubes
136 were connected to the same indirect condenser (coil-type heat exchanger) that was vertically
137 integrated into the separator. The evaporation rate of the equipment was approximately 27 kg.h⁻¹
138 ¹ for a feed flow rate of 70 kg.h⁻¹ and a heating power of 25.2 kW (Silveira et al., 2015).

139 The experimental setup was adapted from Tanguy et al. (2016). The experiments were
140 performed at an absolute pressure of 0.02 MPa, signifying a water evaporation temperature of
141 60°C throughout the three tubes. The products were preheated to the evaporation temperature
142 passing through a tubular heat exchanger with counterflow hot water. Several successive runs
143 were carried out to obtain concentrates at increasing concentration factors, ranging from an
144 initial raw whey up to a maximal concentration factor close to 8. The mass feed flow rate and
145 the evaporation temperature were kept constant at 70 kg.h⁻¹ and 60°C, respectively, for all trials
146 and runs, whereas the heating power was modified during some trials in order to cover a wide
147 range of concentration factors.

148 The same experimental procedure was applied for the concentration of HAW and LAW. Ten
149 to fifteen samples of each concentrate were taken at the end of each run. They were identified
150 as a function of the type of acid whey (HAW and LAW) and their concentration factor, i.e., the
151 ratio of the DM of the concentrate over the DM of the liquid whey. For example, LAW_{2.5}
152 corresponded to the concentrate of lactic acid whey at a concentration factor of 2.5, i.e. a DM
153 content equal to 153.3 g.kg⁻¹.

154 *2.3 Physico-chemical characterization*

155 The concentrates were diluted at the initial dry matter content of the liquid acid whey for the
156 following analyses: dry matter content, nitrogen content, ash content, total cation and anion
157 contents.

158 2.4.1 *Dry matter content*

159 The dry matter contents (DM) were determined as described by IDF standard 21B (ISO-IDF,
160 1987). Five grams of product mixed with sand were dried in a forced air oven at 105°C for 7 h.
161 The weight loss after drying was considered to be the amount of water lost during the process.
162 The experimental error was $\pm 0.5\%$.

163 2.4.2 *Nitrogen contents*

164 The nitrogen contents of the different fractions of the liquid acid wheys and their respective
165 concentrates were determined: the total nitrogen content (TN), the non-casein nitrogen content
166 (NCN) corresponding to the soluble fraction at pH 4.6, and the non-protein nitrogen content
167 (NPN) corresponding to the soluble fraction after their precipitation. After sample
168 mineralization, the nitrogen contents were determined by the Kjeldhal method as described by
169 IDF standard 20B (ISO-IDF, 1993). A nitrogen-to-milk protein conversion factor of 6.38 was
170 used. The experimental errors were $\pm 1\%$ for TN and $\pm 2\%$ for NCN and NPN.

171 The difference between the NCN and NPN contents provides an estimation of the concentration
172 of native whey proteins and gives some indication about the thermal load applied to the products
173 during the industrial processes. The reference value is the concentration of native whey proteins
174 in raw milk that is closed to 7 g.kg⁻¹ (Walstra, Wouters, & Guerts, 2006).

175 2.4.3 *Ash*

176 The ash contents were determined as described by IDF standard 27 (ISO-IDF, 1964). The
177 method consisted of sample incineration (10 g of product) at 550°C for 5 h in a muffle furnace
178 and of the weight of the residue obtained. The experimental error was $\pm 0.5\%$.

179 2.4.4 *pH*

180 The pH of the products were measured at about 22°C using a pH meter with an experimental
181 error of ± 0.02 units.

182 2.4.5 *Concentration of cations and anions*

183 Cation (calcium, sodium, potassium, magnesium) and anion (inorganic phosphate, citrate,
184 chloride) contents were evaluated in the initial wheys, the concentrates and their respective
185 ultrafiltrates. These latter were obtained by ultrafiltration of the products (15 g) on an analytical
186 membrane (molecular weight cut-off: 10 kg.mol⁻¹; Vivaspin, Palaiseau, France) using
187 centrifugation for 1.5 hours at 1800 g at 20°C.

188 The increasing viscosity of the concentrates and the precipitation of components into the
189 concentrates affected the efficiency of the analytical ultrafiltration to recover the diffusible
190 phase. As a consequence, only small volumes of ultrafiltrate (about 2-3 mg) were recovered for
191 the highly concentrated products. Moreover, ion contents were high at high concentration
192 factors, requiring the preparation of very diluted solutions for analysis in the range of calibration
193 of the equipment. Experimental errors were then higher for these highly concentrated products.
194 Cation contents were determined using atomic absorption spectrometry (220FS spectrometer;
195 Varian, France), whereas anion contents were determined using ion exchange chromatography
196 (IEC, Dionex-500; France) (Gaucheron et al., 1996) . Experimental errors were $\pm 2\%$ and $\pm 5\%$
197 for atomic absorption spectrometry and ion chromatography, respectively.

198 The presence of a precipitate in a concentrate led to the formation of a deposit layer on the
199 membrane that generated an exclusion volume above the membrane and led to greater ion
200 concentrations in the ultrafiltrates. It is common to apply a correction factor to mineral
201 concentrations found in ultrafiltrate to take the excluded volume into account (Pierre & Brulé,
202 1981; Walstra & Jenness, 1984). In milk, casein micelles and fat contribute to the excluded
203 volume, and the correction factor applied to mineral concentrations in ultrafiltrate is 0.96
204 (Gaucheron, 2005). In our study, the correction factor was specific to each concentrate since
205 the volume excluded was related to the volume of precipitate formed in highly concentrated
206 products. It was calculated from the ratio of the total ion concentration to the diffusible ion
207 concentration for sodium, magnesium and potassium ions because they generally remain

208 soluble and do not contribute to mineral precipitate in dairy equipment. Finally, a correction
209 factor ranging from 0.88 to 0.99 was applied to the mineral concentrations in the HAW
210 ultrafiltrates whose concentration factors were greater than or equal to 3.9 and for which
211 significant precipitates were observed.

212 *2.4.6 Determination of the composition of the deposit inside the evaporator and the* 213 *precipitate in the concentrates*

214 The composition of the deposit was deduced from the comparison between experimental
215 concentrations of each component and their theoretical ones. The theoretical concentration of a
216 component in a concentrate, referred to as calculated value, was obtained by multiplying the
217 experimental concentration in the liquid acid whey by the concentration factor of the
218 concentrate. An experimental concentration lower than the calculated concentration indicated
219 a loss of this component through deposition on the inside of the evaporator.

220 In the same way, the nature of the species precipitated in the concentrate was deduced from the
221 experimental total ion concentration and the experimental diffusible ion concentration. For a
222 given ion, a diffusible concentration lower than the total concentration indicated its
223 precipitation in the concentrate.

224 *2.4.7 Statistical analysis*

225 Three HAW concentration trials and two LAW concentration trials were carried out. During
226 the first trial, the heating power was kept constant and equal to the maximum heating power
227 (25.2 kW). The heating power of each run was adapted during the second trial in order to reach
228 the concentration factors 2, 3 and 4 and, finally, the maximum achievable concentration factor.
229 This second trial was done in duplicate only in the case of HAW. For a given component, the
230 experimental results of all trials were plotted on the same graph in order to reveal the evolution
231 of its concentration as a function of the concentration factor during vacuum concentration.

232

233 3. Results and discussion

234 3.1 Initial composition of the acid wheys

235 The average compositions of HAW and LAW (Table 1) were in accordance with the literature
236 (Pearce, 1992; Sottiez, 1990). Both had a low pH of around 4.4-4.6, a DM content close to 60
237 g.kg⁻¹, and ash and protein contents in the range of 11-14% w/w DM. These features are specific
238 to acid wheys.

239 The concentration of whey proteins was equal to 7.0 ± 0.4 g.kg⁻¹ in HAW and 3.2 ± 0.3 g.kg⁻¹
240 in LAW, respectively, it can be deduced that HAW received a low thermal load during the
241 production process such as a mild pasteurization, whereas LAW were subjected to more
242 intensive heat treatments. Moreover, the quite high value of NPN in LAW (3.4 g.kg⁻¹ compared
243 to 1.5 g.kg⁻¹ for HAW) could be explained by the presence of proteolytic bacteria in LAW.

244 Regarding the mineral fraction (Table 1), the two acid wheys had concentrations of calcium,
245 sodium, potassium and magnesium in the same range, and the same was true for the inorganic
246 phosphate content. HAW and LAW differed mainly in their chloride, lactate and citrate
247 contents. HAW had a three-fold higher chloride content than LAW due to the addition of
248 hydrochloric acid in milk up to pH 4.6 for casein precipitation. Likewise, LAW had a high
249 lactate content due to the use of lactic bacteria for the preparation of fresh cheeses. Lactic
250 bacteria are known to consume citric acid, leading to the absence of citrate in LAW (Saulnier
251 et al., 1995). On the contrary, citrate is present in HAW at a concentration equivalent to the one
252 found in milk.

253 3.2 Concentration of acid wheys by vacuum evaporation

254 The experimental procedure led to the production of 15 concentrates for HAW and 10
255 concentrates for LAW at different concentration factors. The DM contents reached at the
256 maximum concentration were 431.1 ± 0.2 and 519.3 ± 0.3 g.kg⁻¹ for HAW and LAW,
257 respectively.

258 *3.2.1. Visual observations of the concentrates and the evaporation tubes*

259 Initial HAW and LAW were transparent (Fig. 2) but their concentrates became increasingly
260 turbid during the concentration process. For HAW, a precipitate was present in the concentrates
261 whose concentration factor was greater than or equal to 2.5 and its volume fraction increased
262 with the concentration factor. For LAW, no precipitate was formed in the concentrates whatever
263 the concentration factor.

264 During the concentration of HAW, the formation of a deposit on the inner surface of the
265 evaporation tubes was observed through the porthole. The preheating section was affected as
266 well, with a progressive decrease of the outlet temperature of the concentrate. A higher
267 temperature of the hot water circulating in the jacket of the heat exchanger was applied to
268 maintain an outlet temperature of 60°C. The deposit became thicker with higher concentrations
269 and was present in the three evaporation tubes, especially the third one. At the end of the
270 experiment, its inner surface was covered with a brittle, white deposit.

271 During concentration of LAW, no deposit was formed on the inner surface of the evaporation
272 tubes.

273 *3.3 pH*

274 As expected, the pH of the concentrates decreased during concentration (Singh & Newstead,
275 1992; Walstra et al., 2006). However, it was not to the same extent for both types of whey (Fig.
276 3). The pH decrease was about 1.1 for HAW up to concentration factor 7.6 compared to 0.2 for
277 LAW up to concentration 8.5. The lactate ions, highly present in LAW (9771 mg.kg⁻¹ in LAW₁)
278 contributed to the buffering capacity of the concentrates. Associated to less salt precipitation
279 during LAW concentration, it can explain this low pH evolution.

280 *3.4 Nitrogen fractions*

281 The TN contents of HAW increased linearly with the concentration factor, from 8.4 ± 0.2 g.kg⁻¹
282 ¹ in HAW₁ to 63.0 ± 0.0 g.kg⁻¹ in HAW_{7.6}. Both the experimental and calculated curves were

283 superimposed (Fig. 4), meaning that whey proteins remained in the concentrate without loss of
284 proteins in the evaporator. A similar trend was observed for the NPN content. Regarding the
285 NCN content, it increased linearly with the concentration factor up to HAW_{4.0}. For HAW_{7.6}, the
286 experimental NCN content was slightly lower than the calculated one ($54 \pm 0.1 \text{ g.kg}^{-1}$ and 64
287 g.kg^{-1} respectively), which could not be due to a loss of NCN in the evaporator because the
288 experimental TN content of HAW_{7.6} (including the NCN content) would have been lower than
289 the calculated one. Another reason could be the aggregation of whey proteins due to the
290 combined effects of concentration and heat treatment in the evaporator.
291 Although a greater discrepancy of the NCN values was observed for the LAW concentrates, no
292 loss of proteins in the evaporator could be deduced (Fig. 5).

293 *3.5 Ash content*

294 For HAW, the ash content increased linearly with the concentration factor, from $7.6 \pm 0.0 \text{ g.kg}^{-1}$
295 ¹ in HAW₁ to $29.9 \pm 0.1 \text{ g.kg}^{-1}$ in HAW_{4.0} (Fig. 4). The experimental ash content in HAW_{7.6}
296 was lower than the calculated one (54.5 g.kg^{-1} and 57.7 g.kg^{-1} respectively), which indicated
297 some losses in the evaporator. The quite high relative mean error of the initial ash content in
298 LAW₁ affected the drawing of the theoretical line and the position of the experimental values
299 regarding this line (Fig. 5). It therefore did not make it possible to clearly deduce the loss or not
300 of ash during LAW concentration from these experimental values.

301 *3.6 Calcium, inorganic phosphate, citrate and lactate contents*

302 The main components of deposits in heat exchangers and falling film evaporators are calcium
303 salts, especially calcium phosphate and calcium citrate tetrahydrate (Jeurnink, Walstra, &
304 deKruif, 1996; Jeurnink & Brinkman, 1994; Vavrusova & Skibsted, 2016). Both salts have
305 decreasing solubility with increasing temperature, known as reverse solubility, and are more
306 susceptible to contribute to mineral deposition on heating surfaces (Boulet & Marier, 1960;
307 Vavrusova et al., 2017; Vavrusova & Skibsted, 2016). We therefore focused on the evolution

308 of total and diffusible contents of calcium, inorganic phosphate and citrate during vacuum
309 evaporation. The evolution of lactate contents was also determined since it was present in LAW
310 and might interact with calcium to form calcium lactate.

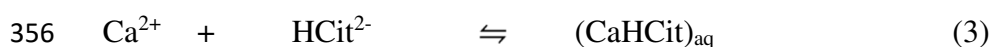
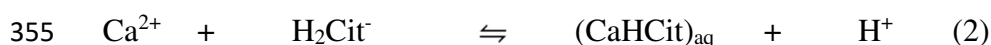
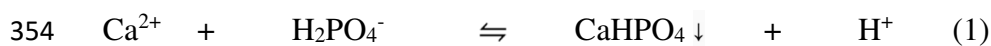
311 *3.6.1. HAW*

312 During the concentration of HAW, the total calcium content increased linearly with the
313 concentration factor up to $HAW_{2.5}$. Beyond this concentration, the experimental values were
314 lower than the calculated ones (Fig. 6). We deduced that some of the calcium ions of the
315 concentrate were deposited in the evaporator as of a concentration factor exceeded 2.5.
316 Moreover, calcium ions may react with inorganic phosphate and citrate ions. The total inorganic
317 phosphate content increased linearly with the concentration factor over the entire range studied
318 suggesting no loss of this ion. On the contrary and similarly to the evolution of calcium ions,
319 the total citrate content increased linearly with the concentration factor up to $HAW_{2.5}$, after
320 which the experimental values were lower than the calculated ones. The experimental
321 concentration for $HAW_{7.6}$ was 33 mmol.kg^{-1} compared to 57 mmol.kg^{-1} for the calculated value,
322 suggesting that a large part of the citrate ions in the concentrates was deposited in the
323 evaporator. These analytical results were in accordance with the visual observations of fouling
324 made during the experiments, i.e., the presence of a brittle, white deposit on the inner surface
325 of the evaporation tubes, characteristic of a mineral deposit (Morison & Thorpe, 2002)

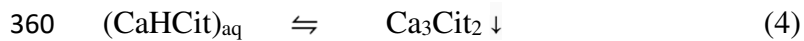
326 During HAW concentration, the diffusible calcium content in the concentrates followed a trend
327 similar to that of the total calcium content. Before concentration, it was equal to the total
328 calcium content and then increased linearly with the concentration factor up to 2.5. Beyond this
329 concentration, it was lower than the experimental and calculated total contents, indicating that
330 part of the calcium corresponding to the difference between the experimental total and
331 diffusible contents was insolubilized at this concentration factor. Regarding inorganic
332 phosphate, the diffusible content was found to be either equal to or slightly higher than the total

333 content due to experimental errors during the preparation of the sample (ultrafiltration and
 334 dilution) and the analysis (ion chromatography). Despite these experimental errors, the results
 335 suggested that no insolubilization of inorganic phosphate ions occurred in the concentrates. On
 336 the contrary and as shown in Fig. 6, the diffusible citrate contents were lower than the total
 337 contents for concentration factors over 2.5. As for calcium ions, the totality of citrate ions could
 338 be considered as soluble up to HAW_{2.5}, whereas 23 mmol.kg⁻¹ were precipitated in HAW_{7.6}.
 339 In the case of HAW, experimental results suggested a deposition of calcium and citrate ions in
 340 the evaporator and the precipitation of both ions in the concentrate for concentration factors
 341 over 2.5. Inorganic phosphate ions were not involved in the formation of the deposit and the
 342 precipitate. These results can be explained in terms of the pH of the concentrates and the
 343 association constants of the ionic forms present. The values for the association constants of the
 344 salt equilibria given by Holt, Dalgleish, & Jenness (1981) provide partial indications about the
 345 preferential reactions that should occur in the evaporator. Indeed, they were determined in milk
 346 diffusate at equilibrium, pH 6.7 and 20-25°C, whereas in our case, the operating temperature
 347 was about 60°C. Moreover and as already mentioned, the concentration factor influenced the
 348 ionic strength and the ionic activity coefficients. Finally, equilibrium conditions were not
 349 reached in the evaporator (Jeurnink & Brinkman, 1994)

350 The pH of the concentrates beyond HAW_{2.5} were in the range of 3.44-4.31. At these pH values,
 351 inorganic phosphate and citrate ions might exist, mainly in their ionized form, H₂PO₄⁻ and
 352 H₂Cit⁻/HCit²⁻, respectively. In milk diffusate conditions, calcium may react with these anions
 353 according to the following reactions:



357 where CaHPO_4 is a poorly soluble salt and $(\text{CaHCit})_{\text{aq}}$ is a soluble complex ion (Boulet &
358 Marier, 1960). When saturation conditions are reached, $(\text{CaHCit})_{\text{aq}}$ would precipitate according
359 to the reaction:



361 The solubility of calcium citrate is also considered as low. Vavrusova et al. (2016) studied its
362 solubility in water from 0 to 100°C. Calcium citrate may exist in tetrahydrate or hexahydrate
363 form, the former being the thermodynamic stable form. Calcium citrate tetrahydrate showed
364 decreasing solubility with increasing temperature, from 6.41 mM at 0°C to 2.82 mM at 100 °C,
365 while the solubility of calcium citrate hexahydrate increased up to the transition temperature
366 (51.6°C) between the two hydrated forms.

367 By considering these informations, reaction (3) should be favored because the association
368 constant between calcium and HCit^{2-} ($K_a=876 \text{ M}^{-1}$) is stronger than the association constants
369 of calcium with H_2PO_4^- ($K_a=21 \text{ M}^{-1}$) and H_2Cit^- ($K_a=28 \text{ M}^{-1}$). The preferential reaction between
370 calcium and citrate might occur at the expense of inorganic phosphate ions.

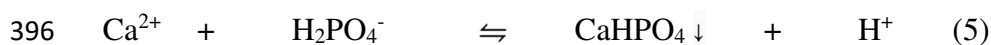
371 The calculated calcium/citrate molar ratios in the deposit and the precipitate for $\text{HAW}_{7.6}$ were
372 1.6 and 2.8, respectively. These values are close to that of calcium citrate salt Ca_3Cit_2 (1.5) for
373 the deposit, and obviously different for the precipitate. Nevertheless, it is very hypothetical to
374 discuss the form of the calcium citrate salt on the sole basis of the calcium/citrate molar ratio.
375 Indeed, the non-equilibrium conditions and the eventual insolubilization of other ionic forms
376 such as a direct deposition of the soluble calcium citrate complex on the heating surfaces might
377 interfere with the forms of the salts deposited and precipitated.

378 The presumed insolubilization of calcium and citrate in the concentrates beyond $\text{HAW}_{2.5}$ was
379 in accordance with the mineral precipitation visually observed in the more concentrated
380 products (Fig. 2).

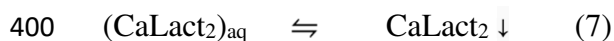
381 *3.6.2. LAW*

382 During LAW concentration, the total calcium, inorganic phosphate and lactate contents
383 increased linearly with the concentration factor over the range studied (Fig. 7). These results
384 suggested that no mineral deposition occurred in the evaporator during vacuum evaporation of
385 LAW, in agreement with the visual observation of the evaporation tubes after experiments. In
386 the same way, diffusible calcium, inorganic phosphate and lactate contents were similar to total
387 experimental contents. They increased linearly with the concentration factor, confirming, as
388 shown in Fig. 2, that no precipitation of minerals occurred over the entire range of concentration
389 factors studied.

390 As previously achieved in the case HAW, the pH of the concentrates and the association
391 constants of salt equilibria given by Holt et al. (1981) provided some information about the
392 preferential interactions that should occur during the concentration process. The pH of the
393 highly concentrated products were in the range of 4.22-4.34. At these pH values, the inorganic
394 phosphate and lactate ions might exist in their ionized forms, H_2PO_4^- and Lact^- , respectively.
395 Calcium may then react with both ions according to the following reactions:



398 where CaHPO_4 is a poorly soluble salt and $(\text{CaLact}_2)_{\text{aq}}$ is a soluble complex ion. When
399 saturation conditions are reached, $(\text{CaLact}_2)_{\text{aq}}$ would precipitate according to the reaction:



401 In milk diffusate conditions, reactions (5) and (6) present roughly similar association constants,
402 21 and 15 M^{-1} , respectively. However, since the concentration of lactate ions is higher than the
403 concentration of inorganic phosphate ions (in the range 500-900 and 100-200 mmol.kg^{-1}
404 respectively), the association of calcium and lactate should be favored at the expense of that of
405 calcium and inorganic phosphate. Moreover, calcium lactate is a moderately soluble salt whose
406 solubility increases with temperature (about 6 g of anhydrous $\text{CaLact}_2/100 \text{ g}$ of water at 24°C)

407 (Kubantseva, Hartel, & Swearingen, 2004), and the threshold concentration of reaction (7) was
408 not exceeded here, as shown by the absence of the precipitate in the concentrated LAW (Fig.
409 2).

410 *3.7 Sodium, potassium, chloride and magnesium contents*

411 Monovalent ions (sodium, potassium, chloride) and divalent magnesium contents were also
412 determined in the different concentrates and their respective diffusible phases (Table 2 for
413 HAW and Table 3 for LAW). There was some discrepancy in the experimental results for the
414 LAW concentration trials. As an example, the mineral composition in the diffusible phase of
415 the more concentrated product (LAW_{8.5}) could not be determined due to the small quantity of
416 ultrafiltrate recovered. However, the numerous data roughly indicated the same trend for these
417 ions regardless of the type of whey, i.e., a linear evolution of the total and diffusible contents
418 with the concentration factor. This suggests that these ions were not insoluble in HAW and
419 LAW concentrates.

420

421 **Conclusions**

422 Selecting the appropriate cleaning strategy of falling film evaporators requires an understanding
423 of the fouling phenomena and knowledge of the nature of the deposit formed. However, the
424 specific design of the evaporators characterized by high and narrow tubes and operation under
425 vacuum makes it difficult to recover and further analyze deposits. In this study, we deduced the
426 nature of the deposits formed in a pilot-scale falling film evaporator on the basis of the
427 experimental determination of the composition of acid whey concentrates at different
428 concentration factors. Hydrochloric acid whey (HAW) and lactic acid whey (LAW) are strongly
429 mineralized but they differ from their mineral composition: HAW contains citrate and no
430 lactate, whereas LAW contains a high level of lactate and traces of citrate.

431 Results showed that concentration of HAW was characterized by fouling of the evaporator and
432 insolubilization in the concentrates, where both phenomena involved calcium and citrate at the
433 expense of inorganic phosphate. In contrast, no deposit or insolubilization occurred during the
434 concentration of LAW. This study underlines the key role of citrate in the fouling of falling film
435 evaporators during the concentration of HAW. The next step is the recovery of the deposit
436 formed inside the evaporator. A direct analysis of the deposit will complete these results of this
437 study, providing information on its structure.

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528

Figure 1. Scheme of the pilot-scale falling-film evaporator (adapted from Silveira et al., 2015)

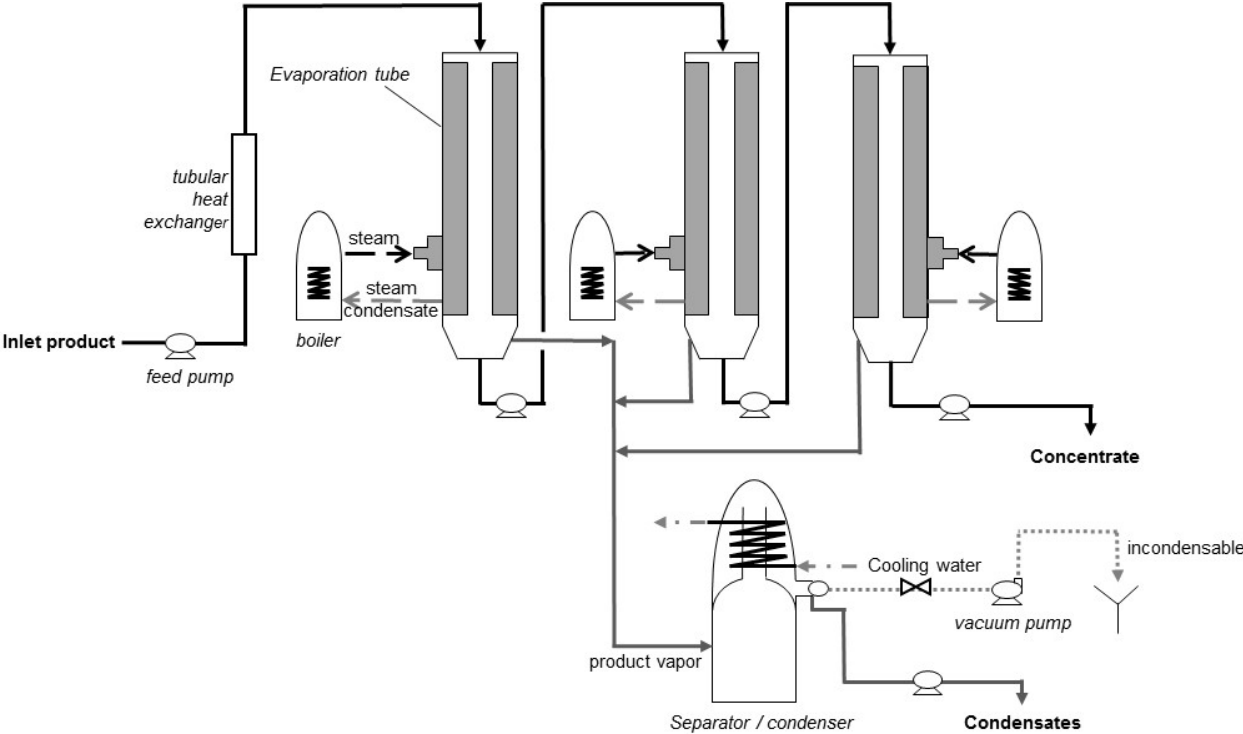


Figure 2. Visual aspect of liquid acid wheys and their concentrates (a: HAW; b: LAW) obtained during trials at constant heating power. The subscripts correspond to the concentration factor.

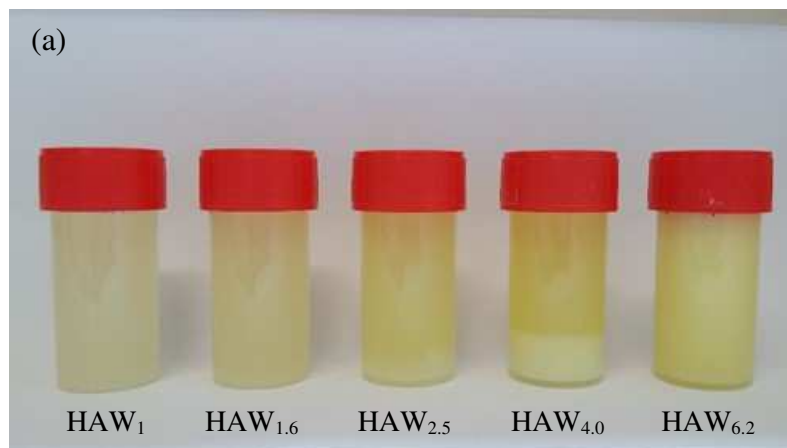


Figure 3. pH of the concentrates of HAW (+) and LAW (o) produced using vacuum evaporation.

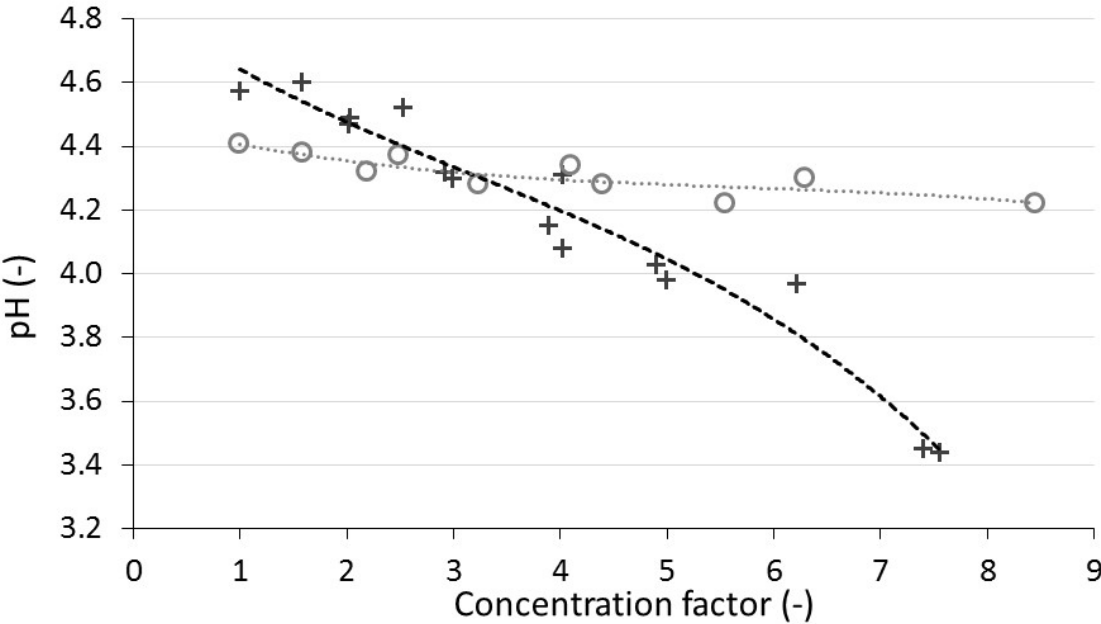
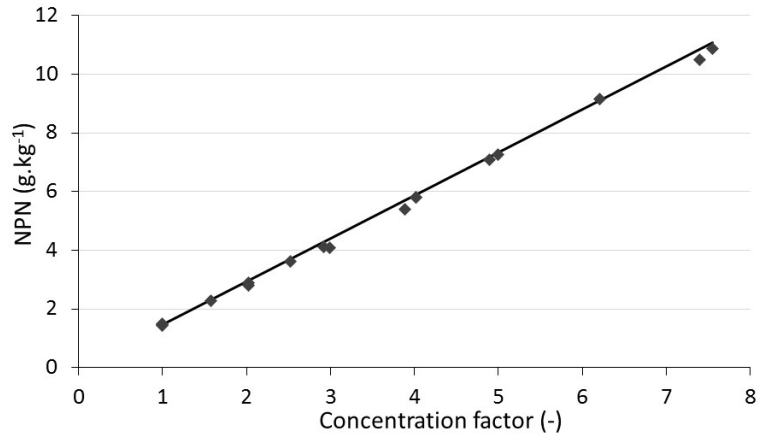
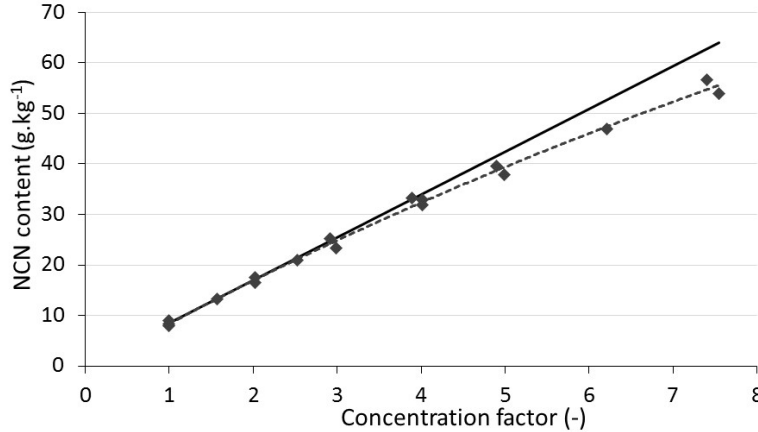
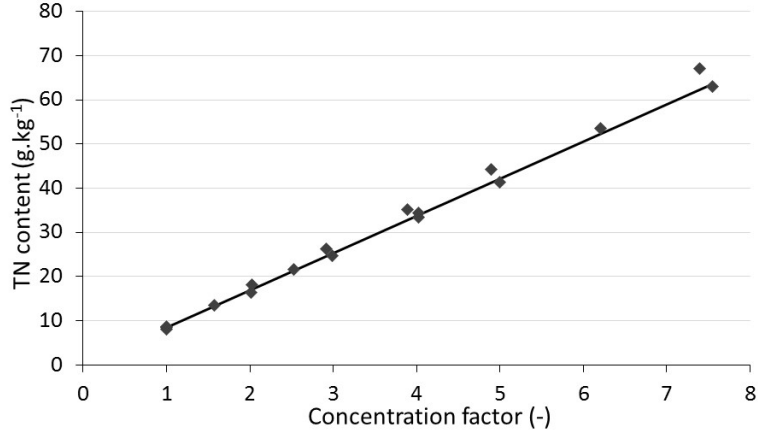


Figure 4. Evolution of TN, NCN, NPN and ash contents as a function of the concentration factor during vacuum evaporation of HAW. Experimental values (symbol \blacklozenge) are compared to the calculated values (solid line). The dotted line refers to the trend line of experimental points.



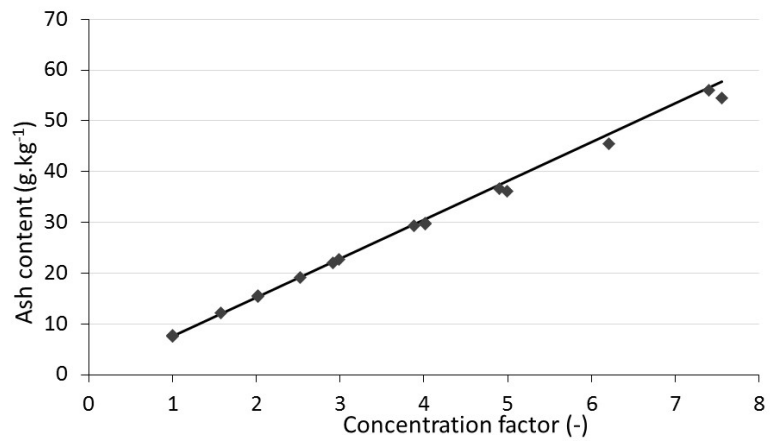
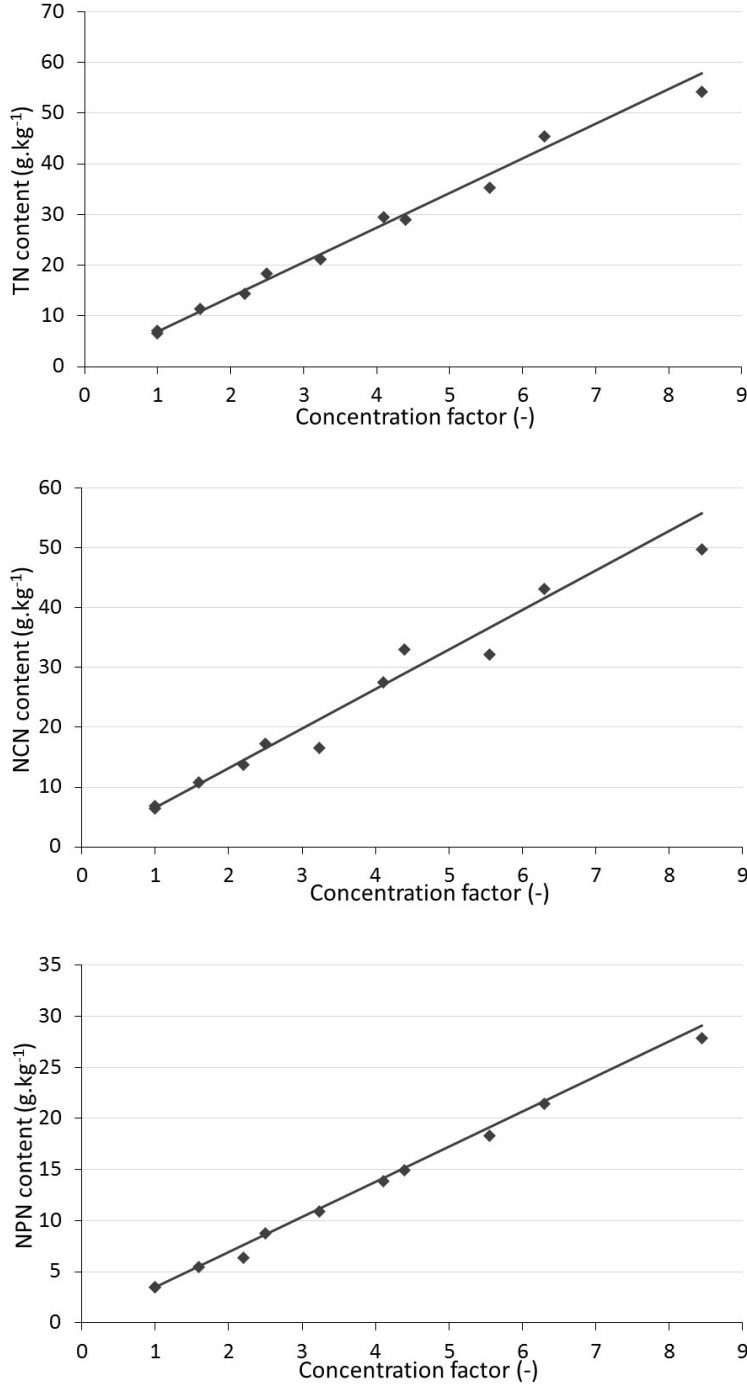


Figure 5. Evolution of TN, NCN, NPN and ash contents as a function of the concentration factor during vacuum evaporation of LAW. Experimental values (symbol \blacklozenge) are compared to the calculated values (solid line). The dotted line refers to the trend line of experimental points.



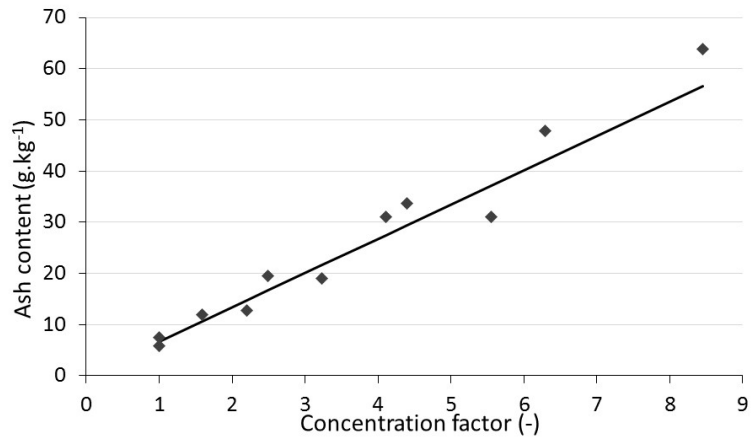


Figure 6. Evolution of the calcium, inorganic phosphate and citrate contents as a function of the concentration factor during vacuum evaporation of HAW. The symbols \blacklozenge and \blacktriangle correspond to the total and soluble experimental contents, respectively. The experimental contents are compared to the calculated values (solid line). Dotted lines refer to the trend lines of experimental points.

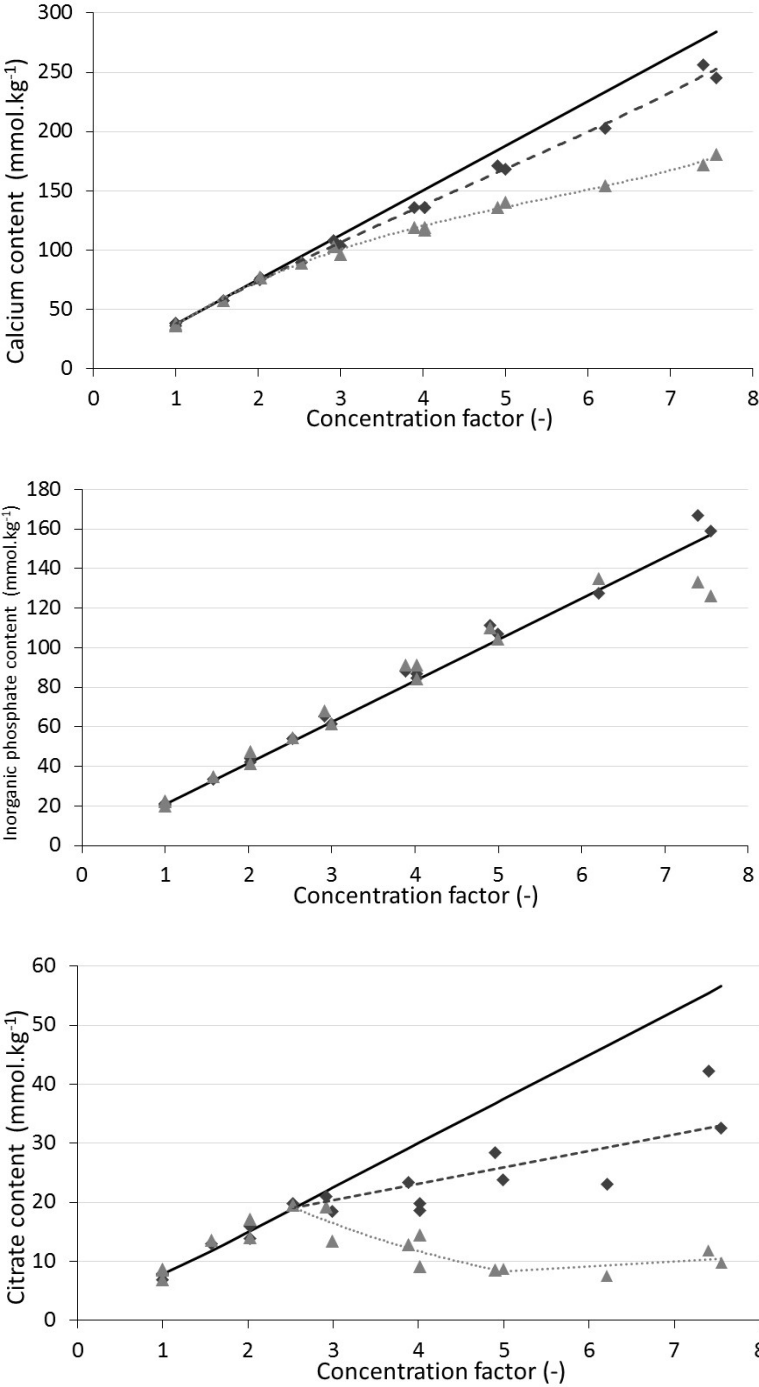


Figure 7. Evolution of the calcium, inorganic phosphate and lactate contents as a function of the concentration factor during vacuum evaporation of LAW. The symbols \blacklozenge and \blacktriangle correspond to the total and soluble experimental contents, respectively. The experimental contents are compared to the calculated values (solid line). Lactate ion content could not be determined in LAW_{8.5} due to its high level.

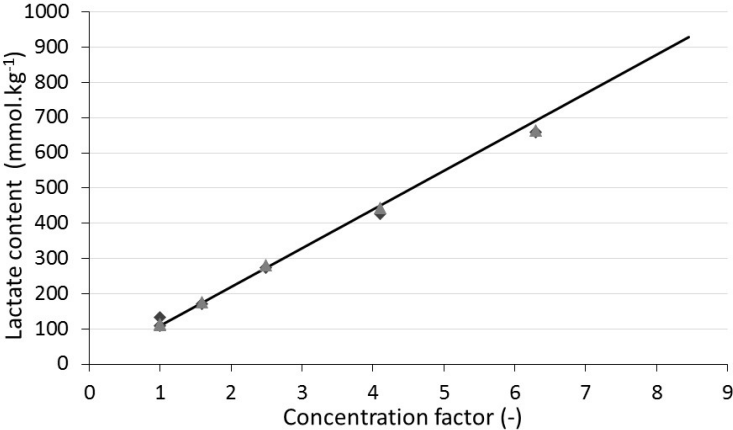
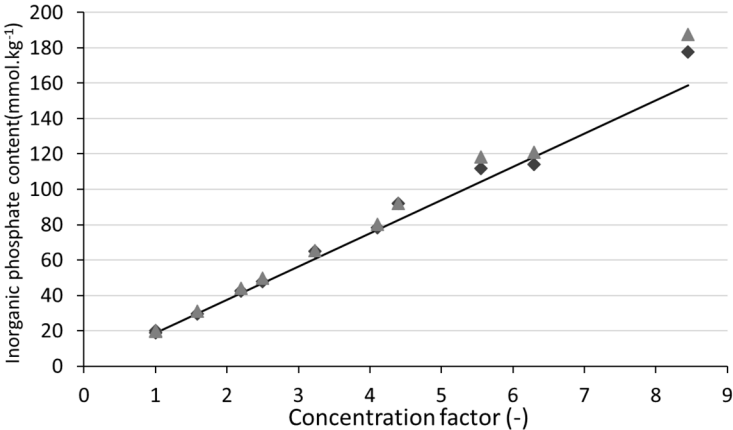
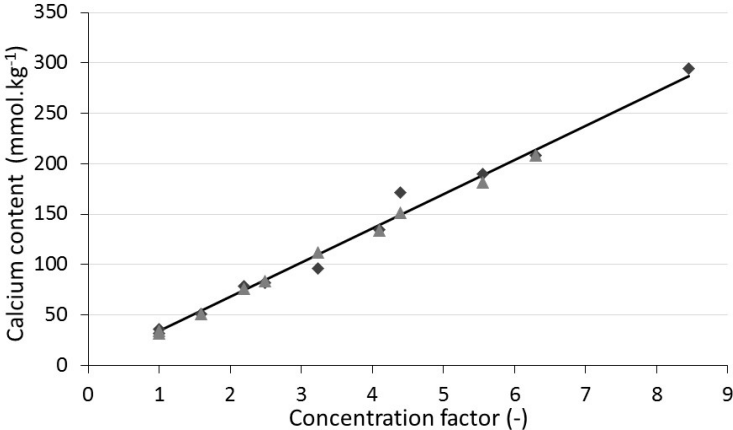


Table 1: Average composition of initial hydrochloric acid whey (HAW) and lactic acid whey (LAW). Values are means \pm standard deviation of all samples of initial raw materials for a product type (three samples for HAW and two for LAW).

	HAW	LAW
pH	4.57 \pm 0.10	4.41 \pm 0.00
Dry matter (g.kg ⁻¹)	58.7 \pm 1.3	61.3 \pm 0.1
Total nitrogen (g.kg ⁻¹)	8.4 \pm 0.2	6.8 \pm 0.3
Non-casein nitrogen (g.kg ⁻¹)	8.5 \pm 0.4	6.6 \pm 0.2
Non-protein nitrogen (g.kg ⁻¹)	1.5 \pm 0.0	3.4 \pm 0.0
Ashes (g.kg ⁻¹)	7.6 \pm 0.0	6.7 \pm 0.9
Total calcium (g.kg ⁻¹)	1.51 \pm 0.03	1.36 \pm 0.08
Total sodium (g.kg ⁻¹)	0.34 \pm 0.01	0.42 \pm 0.03
Total potassium (g.kg ⁻¹)	1.45 \pm 0.04	1.79 \pm 0.06
Total magnesium (g.kg ⁻¹)	0.12 \pm 0.00	0.12 \pm 0.01
Total chloride (g.kg ⁻¹)	3.03 \pm 0.12	0.97 \pm 0.06
Total citrate (g.kg ⁻¹)	1.42 \pm 0.08	< 0.02
Total inorganic phosphate (g.kg ⁻¹)	1.97 \pm 0.03	1.79 \pm 0.05
Total lactate (g.kg ⁻¹)	n.d.	9.77 \pm 0.99

n.d: not detected

Table 2. Total and diffusible contents of monovalent ions (sodium, potassium, chloride) and divalent magnesium in initial HAW and its corresponding concentrates.

CF	Na (mmol.kg ⁻¹)		K (mmol.kg ⁻¹)		Cl (mmol.kg ⁻¹)		Mg (mmol.kg ⁻¹)	
	Total	Diffusible	Total	Diffusible	Total	Diffusible	Total	Diffusible
1	15	15	37	37	85	83	5	5
2	31	31	75	78	176	173	10	10
3	45	45	112	114	257	261	14	14
4	61	63	150	156	357	345	20	20
5	77	78	189	191	443	410	25	24
7.5	118	117	283	289	668	623	37	37

CF: concentration factor

Table 3. Total and diffusible contents of monovalent ions (sodium, potassium, chloride) and divalent magnesium in initial LAW and its corresponding concentrates.

CF	Na (mmol.kg ⁻¹)		K (mmol.kg ⁻¹)		Cl (mmol.kg ⁻¹)		Mg (mmol.kg ⁻¹)	
	Total	Diffusible	Total	Diffusible	Total	Diffusible	Total	Diffusible
1	18	18	45	43	27	28	5	5
1.6	30	28	69	69	40	42	7	7
2.2	-	38	102	99	61	62	11	11
2.5	44	46	112	112	66	68	12	12
3.2	-	56	128	146	96	93	14	16
4.1	71	73	179	181	108	109	19	19
4.4	90	78	229	198	143	128	25	22
5.6	-	93	253	242	192	167	28	26
6.3	111	114	272	280	157	165	29	30
8.5	170	(*)	401	(*)	252	(*)	44	(*)

CF: concentration factor

(*) Diffusible ion contents could not be determined in LAW_{8.5} due to the insufficient quantity of ultrafiltrate recovered.