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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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- 14 the concentration of hydrochloric acid whey

15 Abstract

When dairy powders are produced, the mineral fraction undergoes strong modifications 16 during the vacuum concentration step, leading to the fouling of falling film evaporators. The 17 objective of this study was to determine the nature of the deposits formed during the vacuum 18 concentration of two fouling and highly mineralized products: hydrochloric acid whey and 19 lactic acid whey. These products mainly differ in terms of their mineral composition: lactic acid 20 whey contains a high level of lactic acid and traces of citrate, whereas hydrochloric acid whey 21 22 contains citrate and no lactic acid. Concentrates at different concentration factors were produced using a pilot-scale falling film evaporator. The compositions of the fouling deposits 23 as well as the precipitates present in the concentrates were deduced from the analytical 24 determination of the composition of the concentrates and their respective diffusible phases. The 25 behavior of the mineral fraction of both acid wheys during concentration was shown to be very 26 different. In the case of hydrochloric acid whey, experimental results suggested a deposition of 27 calcium and citrate ions in the evaporator as well as their precipitation in the highly concentrated 28 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 fouling of evaporators during the concentration of hydrochloric acid wheys. 31

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

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35 **1. Introduction**

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

Fouling is a consequence of the numerous changes that undergo the product components during vacuum evaporation. These changes affect the biochemical, physical and rheological properties of the product itself (Singh & Newstead, 1992; Walstra & Jenness, 1984). Their amplitude are not always proportional to the concentration factor because some effects are offset by others. As an example, the activity of the solutes increases due to the concentration but is not directly proportional to the concentration factor since the increasing ionic strength decreases the activity coefficients. In turn, the reduced activity coefficients lead to an increasein the ionization and solubility of salts (Walstra & Jenness, 1984).

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

Concentration also affects the physical properties (density, refractive index, heat conductivity, 69 etc.) and the rheological properties of concentrates. They become more and more viscous and 70 71 clearly exhibit their non-Newtonian behavior beyond a given DM content (Velez-Ruiz & Barbosa-Canovas, 1997). Viscosity is a key parameter in the operation of falling film 72 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 parameters such as heat treatment before concentration, operating temperature and residence 75 time in the falling film evaporator or storage time after concentration (Singh & Newstead, 76 77 1992).

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

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

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

120 **2.** Materials and Methods

121 *2.1 Initial raw materials*

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

127 2.2 Concentration of both acid wheys at the pilot scale

Both acid wheys were concentrated in a pilot-scale falling film evaporator (GEA Process Engineering, St Quentin-en-Yvelines, France) composed of three evaporation tubes in series (Fig. 1). The evaporator was well-characterized by Silveira et al. (2013) and Silveira et al. (2015). Its configuration was close to those used in the dairy industry, especially from a hydrodynamic point of view. The tubes were 4-m high and had internal diameters of 0.036 m (first tube) and 0.023 m (second and third tubes). A single porthole on the side of the tubes made it possible to inspect the appearance of their inner surfaces. Each of the tubes was equipped with an electric boiler that provided energy for water evaporation. The three tubes were connected to the same indirect condenser (coil-type heat exchanger) that was vertically integrated into the separator. The evaporation rate of the equipment was approximately 27 kg.h⁻¹ for a feed flow rate of 70 kg.h⁻¹ and a heating power of 25.2 kW (Silveira et al., 2015).

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

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

154 *2.3 Physico-chemical characterization*

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

158 2.4.1 Dry matter content

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

The nitrogen contents of the different fractions of the liquid acid wheys and their respective concentrates were determined: the total nitrogen content (TN), the non-casein nitrogen content (NCN) corresponding to the soluble fraction at pH 4.6, and the non-protein nitrogen content (NPN) corresponding to the soluble fraction after their precipitation. After sample mineralization, the nitrogen contents were determined by the Kjeldhal method as described by IDF standard 20B (ISO-IDF, 1993). A nitrogen-to-milk protein conversion factor of 6.38 was 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*

The ash contents were determined as described by IDF standard 27 (ISO-IDF, 1964). The method consisted of sample incineration (10 g of product) at 550°C for 5 h in a muffle furnace 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.

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

The presence of a precipitate in a concentrate led to the formation of a deposit layer on the 198 membrane that generated an exclusion volume above the membrane and led to greater ion 199 concentrations in the ultrafiltrates. It is common to apply a correction factor to mineral 200 concentrations found in ultrafiltrate to take the excluded volume into account (Pierre & Brulé, 201 202 1981; Walstra & Jenness, 1984). In milk, casein micelles and fat contribute to the excluded volume, and the correction factor applied to mineral concentrations in ultrafiltrate is 0.96 203 (Gaucheron, 2005). In our study, the correction factor was specific to each concentrate since 204 205 the volume excluded was related to the volume of precipitate formed in highly concentrated products. It was calculated from the ratio of the total ion concentration to the diffusible ion 206 207 concentration for sodium, magnesium and potassium ions because they generally remain soluble and do not contribute to mineral precipitate in dairy equipment. Finally, a correction
factor ranging from 0.88 to 0.99 was applied to the mineral concentrations in the HAW
ultrafiltrates whose concentration factors were greater than or equal to 3.9 and for which
significant precipitates were observed.

2.4.6 Determination of the composition of the deposit inside the evaporator and the

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precipitate in the concentrates

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

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

224 2.4.

2.4.7 Statistical analysis

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

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3 3. Results and discussion

234 *3.1 Initial composition of the acid wheys*

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

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

in LAW, respectively, it can be deduced that HAW received a low thermal load during the production process such as a mild pasteurization, whereas LAW were subjected to more intensive heat treatments. Moreover, the quite high value of NPN in LAW (3.4 g.kg⁻¹ compared to 1.5 g.kg⁻¹ for HAW) could be explained by the presence of proteolytic bacteria in LAW.

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

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3.2 .Concentration of acid wheys by vacuum evaporation

The experimental procedure led to the production of 15 concentrates for HAW and 10 concentrates for LAW at different concentration factors. The DM contents reached at the maximum concentration were 431.1 ± 0.2 and 519.3 ± 0.3 g.kg⁻¹ for HAW and LAW, respectively. 3.2.1. Visual observations of the concentrates and the evaporation tubes

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

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

During concentration of LAW, no deposit was formed on the inner surface of the evaporationtubes.

273 *3.3 pH*

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

280 *3.4 Nitrogen fractions*

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

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superimposed (Fig. 4), meaning that whey proteins remained in the concentrate without loss of 283 proteins in the evaporator. A similar trend was observed for the NPN content. Regarding the 284 NCN content, it increased linearly with the concentration factor up to HAW_{4.0}. For HAW_{7.6}, the 285 experimental NCN content was slightly lower than the calculated one $(54 \pm 0.1 \text{ g.kg}^{-1} \text{ and } 64$ 286 g.kg⁻¹ respectively), which could not be due to a loss of NCN in the evaporator because the 287 experimental TN content of HAW_{7.6} (including the NCN content) would have been lower than 288 289 the calculated one. Another reason could be the aggregation of whey proteins due to the combined effects of concentration and heat treatment in the evaporator. 290

Although a greater discrepancy of the NCN values was observed for the LAW concentrates, noloss of proteins in the evaporator could be deduced (Fig. 5).

3.5 Ash content

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

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

The main components of deposits in heat exchangers and falling film evaporators are calcium salts, especially calcium phosphate and calcium citrate tetrahydrate (Jeurnink, Walstra, & deKruif, 1996; Jeurnink & Brinkman, 1994; Vavrusova & Skibsted, 2016). Both salts have decreasing solubility with increasing temperature, known as reverse solubility, and are more susceptible to contribute to mineral deposition on heating surfaces (Boulet & Marier, 1960; Vavrusova et al., 2017; Vavrusova & Skibsted, 2016). We therefore focused on the evolution of total and diffusible contents of calcium, inorganic phosphate and citrate during vacuum
evaporation. The evolution of lactate contents was also determined since it was present in LAW
and might interact with calcium to form calcium lactate.

311 *3.6.1. HAW*

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

During HAW concentration, the diffusible calcium content in the concentrates followed a trend similar to that of the total calcium content. Before concentration, it was equal to the total calcium content and then increased linearly with the concentration factor up to 2.5. Beyond this concentration, it was lower than the experimental and calculated total contents, indicating that part of the calcium corresponding to the difference between the experimental total and diffusible contents was insolubilized at this concentration factor. Regarding inorganic phosphate, the diffusible content was found to be either equal to or slightly higher than the total content due to experimental errors during the preparation of the sample (ultrafiltration and dilution) and the analysis (ion chromatography). Despite these experimental errors, the results suggested that no insolubilization of inorganic phosphate ions occurred in the concentrates. On the contrary and as shown in Fig. 6, the diffusible citrate contents were lower than the total contents for concentration factors over 2.5. As for calcium ions, the totality of citrate ions could be considered as soluble up to HAW_{2.5}, whereas 23 mmol.kg⁻¹ were precipitated in HAW_{7.6}.

In the case of HAW, experimental results suggested a deposition of calcium and citrate ions in 339 the evaporator and the precipitation of both ions in the concentrate for concentration factors 340 over 2.5. Inorganic phosphate ions were not involved in the formation of the deposit and the 341 precipitate. These results can be explained in terms of the pH of the concentrates and the 342 association constants of the ionic forms present. The values for the association constants of the 343 salt equilibria given by Holt, Dalgleish, & Jenness (1981) provide partial indications about the 344 345 preferential reactions that should occur in the evaporator. Indeed, they were determined in milk diffusate at equilibrium, pH 6.7 and 20-25°C, whereas in our case, the operating temperature 346 347 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 reached in the evaporator (Jeurnink & Brinkman, 1994) 349

The pH of the concentrates beyond HAW_{2.5} were in the range of 3.44-4.31. At these pH values, inorganic phosphate and citrate ions might exist, mainly in their ionized form, $H_2PO_4^-$ and $H_2Cit^-/HCit^{2-}$, respectively. In milk diffusate conditions, calcium may react with these anions according to the following reactions:

354	Ca ²⁺	+	$H_2PO_4^-$	4	CaHPO ₄ ↓	+	H^+	(1)
355	Ca ²⁺	+	H ₂ Cit ⁻	4	(CaHCit) _{aq}	+	H^{+}	(2)
356	Ca ²⁺	+	HCit ²⁻	4	(CaHCit) _{aq}			(3)

where CaHPO₄ is a poorly soluble salt and (CaHCit)_{aq} is a soluble complex ion (Boulet &
Marier, 1960). When saturation conditions are reached, (CaHCit)_{aq} would precipitate according
to the reaction:

 $360 \quad (CaHCit)_{aq} \quad \leftrightarrows \quad Ca_3Cit_2 \downarrow \tag{4}$

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

By considering these informations, reaction (3) should be favored because the association constant between calcium and HCit²⁻ (Ka=876 M⁻¹) is stronger than the association constants of calcium with $H_2PO_4^-$ (Ka=21 M⁻¹) and H_2Cit^- (Ka=28 M⁻¹). The preferential reaction between calcium and citrate might occur at the expense of inorganic phosphate ions.

The calculated calcium/citrate molar ratios in the deposit and the precipitate for HAW_{7.6} were 1.6 and 2.8, respectively. These values are close to that of calcium citrate salt Ca₃Cit₂ (1.5) for the deposit, and obviously different for the precipitate. Nevertheless, it is very hypothetical to discuss the form of the calcium citrate salt on the sole basis of the calcium/citrate molar ratio. Indeed, the non-equilibrium conditions and the eventual insolubilization of other ionic forms such as a direct deposition of the soluble calcium citrate complex on the heating surfaces might interfere with the forms of the salts deposited and precipitated.

The presumed insolubilization of calcium and citrate in the concentrates beyond $HAW_{2.5}$ was in accordance with the mineral precipitation visually observed in the more concentrated products (Fig. 2).

381 *3.6.2. LAW*

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

As previously achieved in the case HAW, the pH of the concentrates and the association constants of salt equilibria given by Holt et al. (1981) provided some information about the preferential interactions that should occur during the concentration process. The pH of the highly concentrated products were in the range of 4.22-4.34. At these pH values, the inorganic phosphate and lactate ions might exist in their ionized forms, H₂PO₄⁻ and Lact⁻, respectively. Calcium may then react with both ions according to the following reactions:

 Ca^{2+} 396 + $H_2PO_4^-$ 与 CaHPO₄↓ + H^+ (5) 397 Ca^{2+} Lact (CaLact₂)_{aq} + \Leftarrow (6)

398 where CaHPO₄ is a poorly soluble salt and $(CaLact_2)_{aq}$ is a soluble complex ion. When 399 saturation conditions are reached, $(CaLact_2)_{aq}$ would precipitate according to the reaction:

400 $(CaLact_2)_{aq} \Leftrightarrow CaLact_2 \downarrow (7)$

In milk diffusate conditions, reactions (5) and (6) present roughly similar association constants, 21 and 15 M^{-1} , respectively. However, since the concentration of lactate ions is higher than the concentration of inorganic phosphate ions (in the range 500-900 and 100-200 mmol.kg⁻¹ respectively), the association of calcium and lactate should be favored at the expense of that of calcium and inorganic phosphate. Moreover, calcium lactate is a moderately soluble salt whose solubility increases with temperature (about 6 g of anhydrous CaLact₂/100 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

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

420

421 Conclusions

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

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

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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 (0) 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 ◆) 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 ± 0.10	4.41 ± 0.00
Dry matter (g.kg ⁻¹)	58.7 ± 1.3	61.3 ± 0.1
Total nitrogen (g.kg ⁻¹)	8.4 ± 0.2	6.8 ± 0.3
Non-casein nitrogen (g.kg ⁻¹)	8.5 ± 0.4	6.6 ± 0.2
Non-protein nitrogen (g.kg ⁻¹)	1.5 ± 0.0	3.4 ± 0.0
Ashes (g.kg ⁻¹)	7.6 ± 0.0	6.7 ± 0.9
Total calcium (g.kg ⁻¹)	1.51 ± 0.03	1.36 ± 0.08
Total sodium (g.kg ⁻¹)	0.34 ± 0.01	0.42 ± 0.03
Total potassium (g.kg ⁻¹)	1.45 ± 0.04	1.79 ± 0.06
Total magnesium (g.kg ⁻¹)	0.12 ± 0.00	0.12 ± 0.01
Total chloride (g.kg ⁻¹)	3.03 ± 0.12	0.97 ± 0.06
Total citrate (g.kg ⁻¹)	1.42 ± 0.08	< 0.02
Total inorganic phosphate (g.kg ⁻¹)	1.97 ± 0.03	1.79 ± 0.05
Total lactate (g.kg ⁻¹)	n.d.	9.77 ± 0.99

n.d: not detected

Table 2. Total and diffusible contents of monovalent ions (sodium, potassium, chloride) anddivalent 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 (mn	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.