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

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ABSTRACT

When dairy powders are produced, the mineral fraction undergoes strong modifications during the vacuum concentration step, leading to the fouling of falling film evaporators. The objective of this study was to determine the nature of the deposits formed during the vacuum concentration of two fouling and highly mineralized products: hydrochloric acid whey and lactic acid whey. These products mainly differ in terms of their mineral composition: lactic acid whey contains a high level of lactic acid and traces of citrate, whereas hydrochloric acid whey 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 as well as the precipitates present in the concentrates were deduced from the analytical determination of the composition of the concentrates and their respective diffusible phases. The behavior of the mineral fraction of both acid wheys during concentration was shown to be very different. In the case of hydrochloric acid whey, experimental results suggested a deposition of calcium and citrate ions in the evaporator as well as their precipitation in the highly concentrated products. On the contrary, neither mineral deposition nor precipitation occurred during the 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.

1. Introduction

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 formula and as a nutrient in dietetic and health foods. Even though there is a wide variability in their compositions depending on the processing conditions (Saulnier, Ferrero, Bottero, & Linden, 1995), wheys can be further classified into two groups in terms of their acidity. Sweet whey comes from the cheese manufacturing process that uses rennet-type enzymes. Its pH is around 6.4–6.6 and it is composed of water (94% liquid), lactose (75% *w*/w dry matter content, DM), proteins (13% w/w DM), minerals (8–9% w/w DM) and fat (1% w/w DM) (Pearce, 1992). Given its high lactose content and protein composition, sweet whey is commonly spray-dried and used in high-value dairy powders such as those used for infant nutrition. Acid wheys result from the production of acid-coagulated dairy products, including fresh cheeses and caseins. They contain 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 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 and deposit of mineral salts on heating surfaces of falling film evaporators are favored. This deposition of matter on heating surfaces is known as fouling.

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 increase in the ionization and solubility of salts (Walstra & Jenness, 1984).

Concentration has an impact on salt equilibrium since solubility products may be exceeded and salts may then precipitate with

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increasing concentration factors, as is the case for calcium phosphate and calcium citrate (Walstra & Jenness, 1984). This precipitation, combined with an increased ionization of ionic species and the concentration of H^+ ions, induces a decrease in the pH of the solution and an increase in the ratio of monovalent to divalent cations. Concerning proteins, lowering the pH and increasing ionic strength favors their association since it comes with closer packing of molecules, decreasing thickness of the ionic double layer and lower apparent isoelectric pH (Walstra & Jenness, 1984).

Concentration also affects the physical properties (density, refractive index, heat conductivity, etc.) and the rheological properties of concentrates. They become more and more viscous and clearly exhibit their non-Newtonian behavior beyond a given DM content (Velezruiz & Barbosacanovas, 1997). Viscosity is a key parameter in the operation of falling film evaporators since it determines the maximum achievable DM content in this equipment (Gray, 1981). Finally, the changes during vacuum evaporation depend to some extent on other parameters such as heat treatment before concentration, operating temperature and residence time in the falling film evaporator or storage time after concentration (Singh & Newstead, 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. Numerous studies and reviews in the literature deal with the nature and mechanisms of deposition and cleaning procedures (Bansal & Chen, 2006; Changani, Belmar-Beiny, & Fryer, 1997; Jun & Puri, 2005; Sadeghinezhad et al., 2013; Visser & Jeurnink, 1997). On the contrary, few studies have focused on the fouling of falling evaporators. However, it is unlikely that the natures of deposits are similar in falling film evaporators and in heat exchangers (Jeurnink & Brinkman, 1994; Morison, 2015). The use of vacuum, the increasing concentration of compounds, the decreasing temperature in the evaporator and the longer residence times make the operating conditions different from those encountered in heat exchangers. As an example, Jeurnink and Brinkman (1994) observed the presence of protein deposits in falling film evaporators during the concentration of milk although the proteins had been previously denatured in the preheating section. The authors suggested that due to the concentration of dairy 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 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. Moreover, after the concentration of whey from 5 to 28% *w*/w DM, the main components of the deposit were proteins and calcium phosphate, whereas after the concentration of whey from 28 to 55% *w*/w DM, a larger deposit was produced and the main component was calcium citrate. Vavrusova, Johansen, Garcia, and Skibsted (2017) analyzed the composition of a deposit formed during the concentration of whey permeate using infrared spectroscopy and found that the main component was calcium 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 evaporator.

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

Table 1
Average composition of initial hydrochloric acid whey (HAW) and lactic acid whey (LAW). Values are means ± 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.

2. Materials and methods

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.

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 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 passing through a tubular heat exchanger with counterflow hot water. Several successive runs were carried out to obtain concentrates at increasing concentration factors, ranging from an initial raw whey up to a

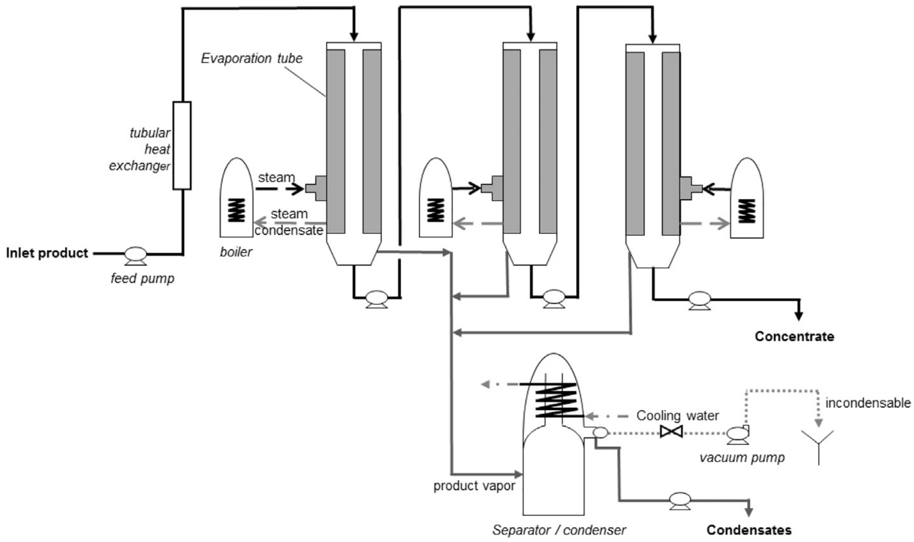

Fig. 1. Scheme of the pilot-scale falling-film evaporator.
Adapted from Silveira et al. (2015).

maximal concentration factor close to 8. The mass feed flow rate and the evaporation temperature were kept constant at 70 kg.h^{-1} and 60 °C, respectively, for all trials and runs, whereas the heating power was modified during some trials in order to cover a wide 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}.

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.

2.3.1. Dry matter content

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

2.3.2. 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 ± 1% for TN and ± 2% for NCN and NPN.

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

2.3.3. 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 ± 0.5%.

2.3.4. pH

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

2.3.5. Concentration of cations and anions

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

The increasing viscosity of the concentrates and the precipitation of components into the concentrates affected the efficiency of the analytical ultrafiltration to recover the diffusible 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 factors, requiring the preparation of very diluted solutions for analysis in the range of calibration of the equipment. Experimental errors were then higher for these highly concentrated products.

Cation contents were determined using atomic absorption spectrometry (220FS spectrometer; Varian, France), whereas anion contents were determined using ion exchange chromatography (IEC, Dionex-500; France) (Gaucheron, Graet, Piot, & Boyaval, 1996). Experimental errors were ± 2% and ± 5% for atomic absorption spectrometry and ion chromatography, respectively.

The presence of a precipitate in a concentrate led to the formation of a deposit layer on the membrane that generated an exclusion volume above the membrane and led to greater ion concentrations in the ultrafiltrates. It is common to apply a correction factor to mineral concentrations found in ultrafiltrate to take the excluded volume into account (Pierre & Brule, 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 (Gaucheron, 2005). In our study, the correction factor was specific to

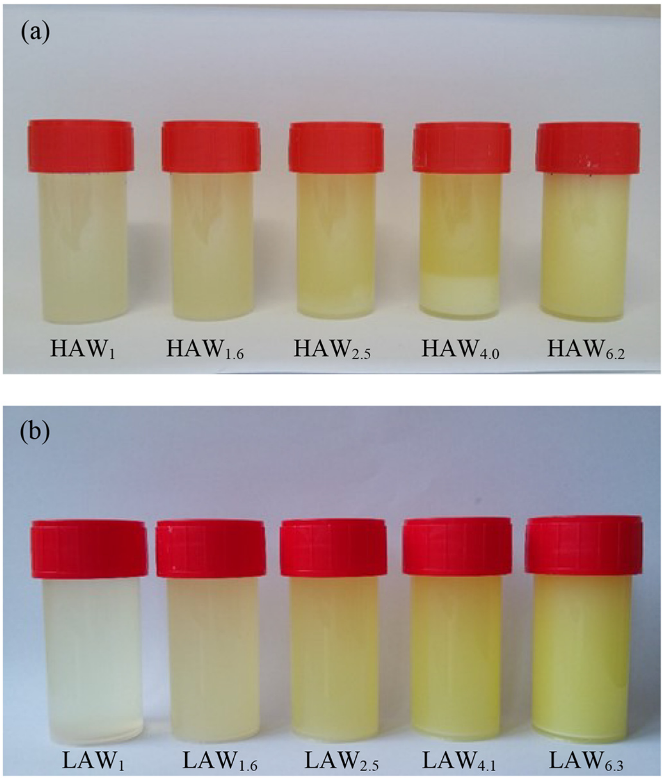

Fig. 2. Visual aspect of liquid acid wheys and their concentrates (a: HAW; b: LAW) obtained during trials at constant heating power. The subscripts correspond to the concentration factor.

each concentrate since 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 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.

2.3.6. *Determination of the composition of the deposit inside the evaporator and the 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.

2.3.7. *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.

3. Results and discussion

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

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 evaporation tubes.

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

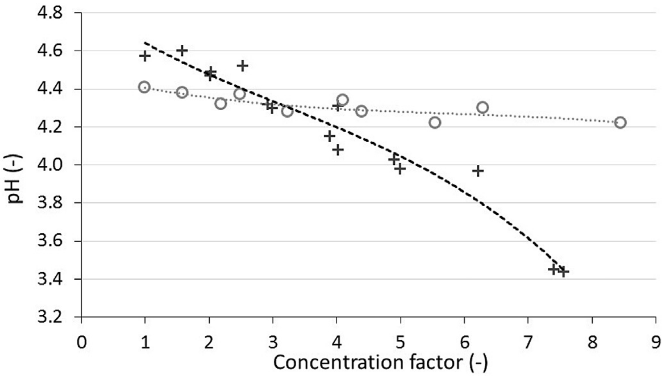

Fig. 3. pH of the concentrates of HAW (+) and LAW (o) produced using vacuum evaporation.

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 LAW$_1$) contributed to the buffering capacity of the concentrates. Associated to less salt precipitation during LAW concentration, it can explain this low pH evolution.

3.4. Nitrogen fractions

The TN contents of HAW increased linearly with the concentration factor, from 8.4 ± 0.2 g.kg^{-1} in HAW$_1$ to 63.0 ± 0.0 g.kg^{-1} in HAW$_{7.6}$. Both the experimental and calculated curves were superimposed (Fig. 4), meaning that whey proteins remained in the concentrate without loss of proteins in the evaporator. A similar trend was observed for the NPN content. Regarding the NCN content, it increased linearly with the concentration factor up to HAW$_{4.0}$. For HAW$_{7.6}$, the experimental NCN content was slightly lower than the calculated one (54.0 ± 0.1 g.kg^{-1} and 64 g.kg^{-1} respectively), which could not be due to a loss of NCN in the evaporator because the experimental TN content of HAW$_{7.6}$ (including the NCN content) would have been lower than 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.

Although a greater discrepancy of the NCN values was observed for the LAW concentrates, no loss 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} in HAW$_1$ 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 LAW$_1$ 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.

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 & Brinkman, 1994; Jeurnink, Walstra, & Dekruif, 1996; 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;

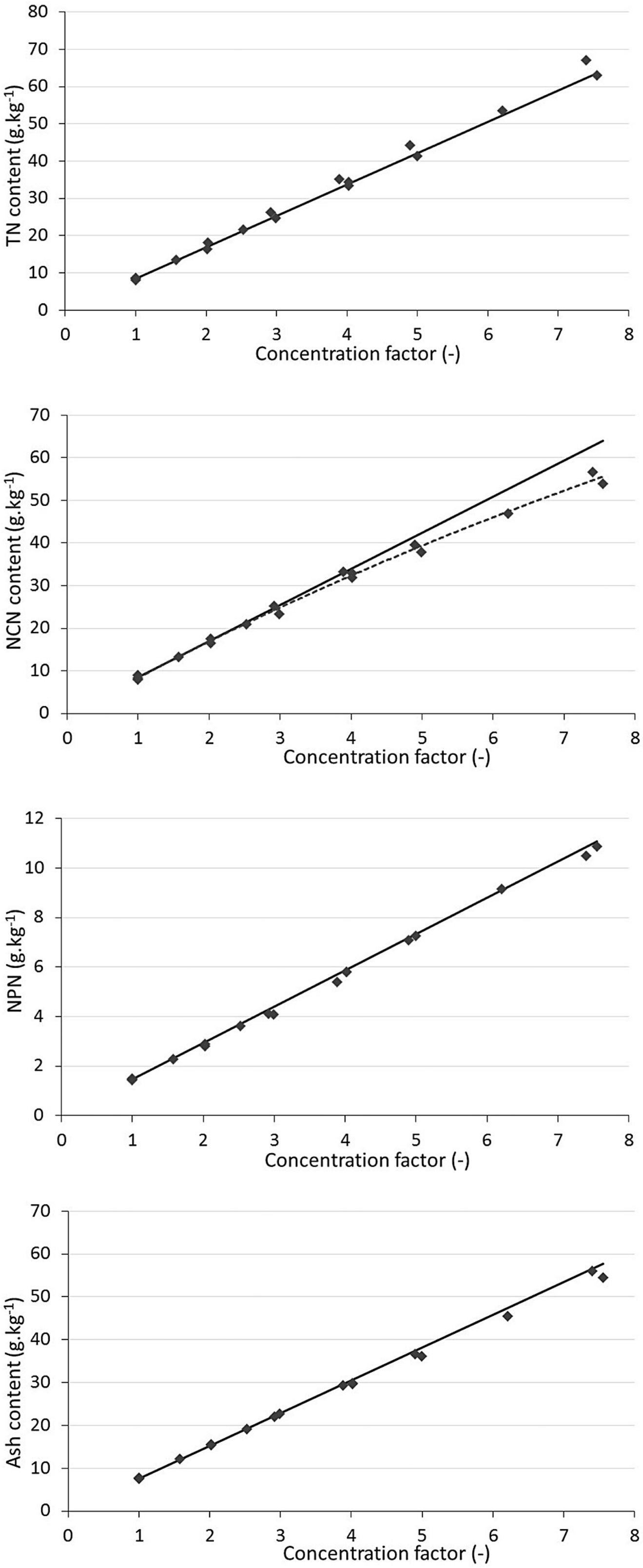

Fig. 4. Evolution of TN, NCN, NPN and ash contents as a function of the concentration factor during vacuum evaporation of HAW. Experimental values (symbol ◆) are compared to the calculated values (solid line). The dotted line refers to the trend line of experimental points.

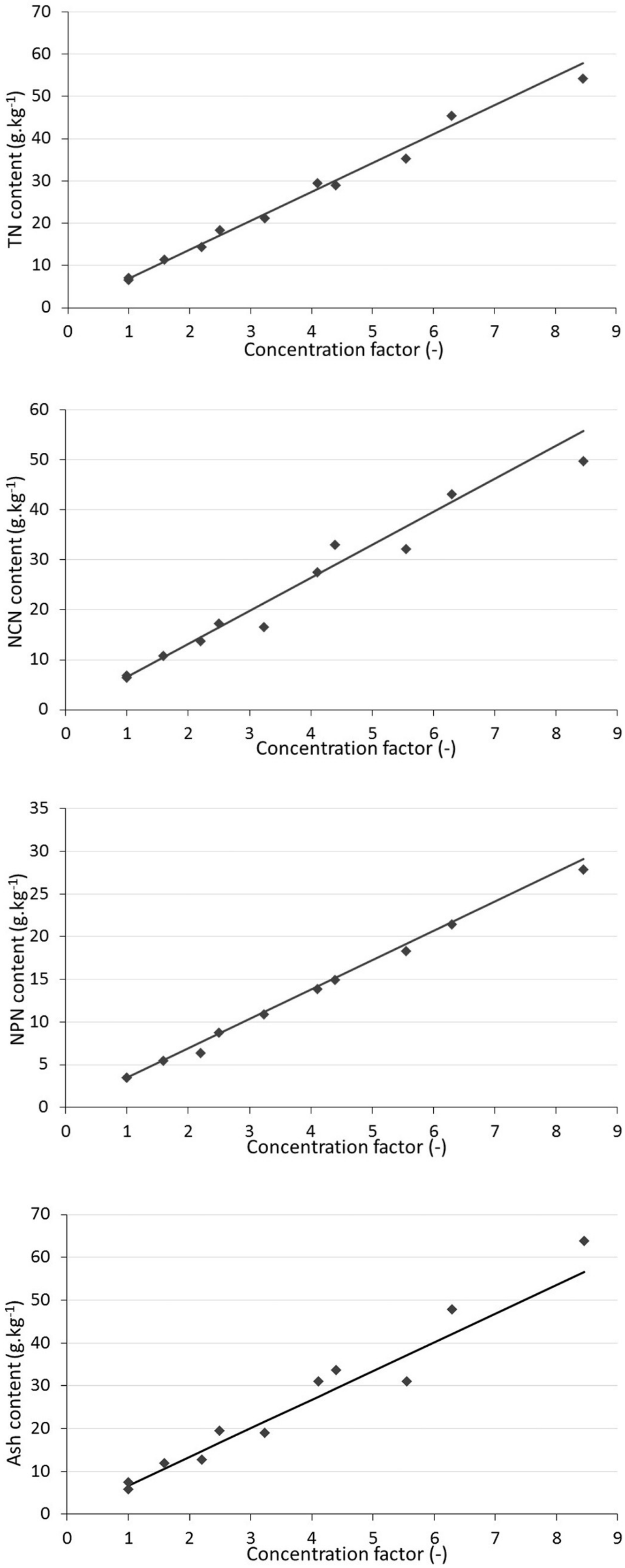

Fig. 5. Evolution of TN, NCN, NPN and ash contents as a function of the concentration factor during vacuum evaporation of LAW. Experimental values (symbol ◆) are compared to the calculated values (solid line). The dotted line refers to the trend line of experimental points.

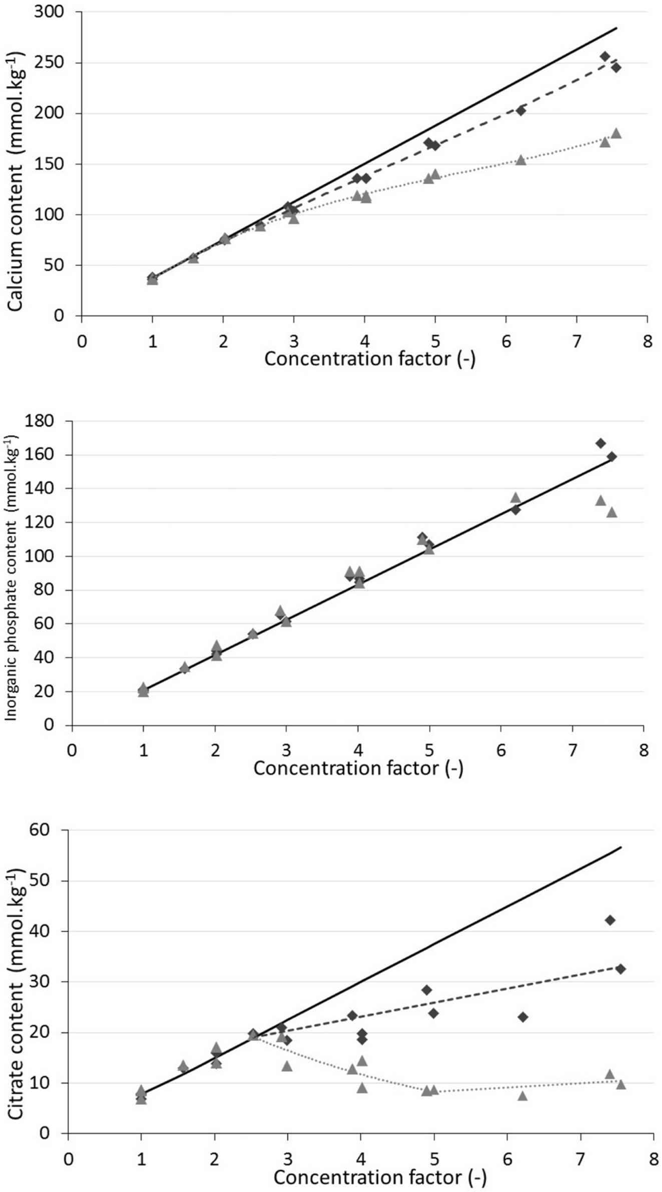

Fig. 6. Evolution of the calcium, inorganic phosphate and citrate contents as a function of the concentration factor during vacuum evaporation of HAW. The symbols ◆ and ▲ correspond to the total and soluble experimental contents, respectively. The experimental contents are compared to the calculated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

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.

3.6.1. HAW

During the concentration of HAW, the total calcium content increased linearly with the concentration factor up to $HAW_{2.5}$. Beyond this concentration, the experimental values were lower than the calculated ones (Fig. 6). We deduced that some of the calcium ions of the concentrate were deposited in the evaporator as of a concentration factor exceeded 2.5. Moreover, calcium ions may react with inorganic phosphate and citrate ions. The total inorganic 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

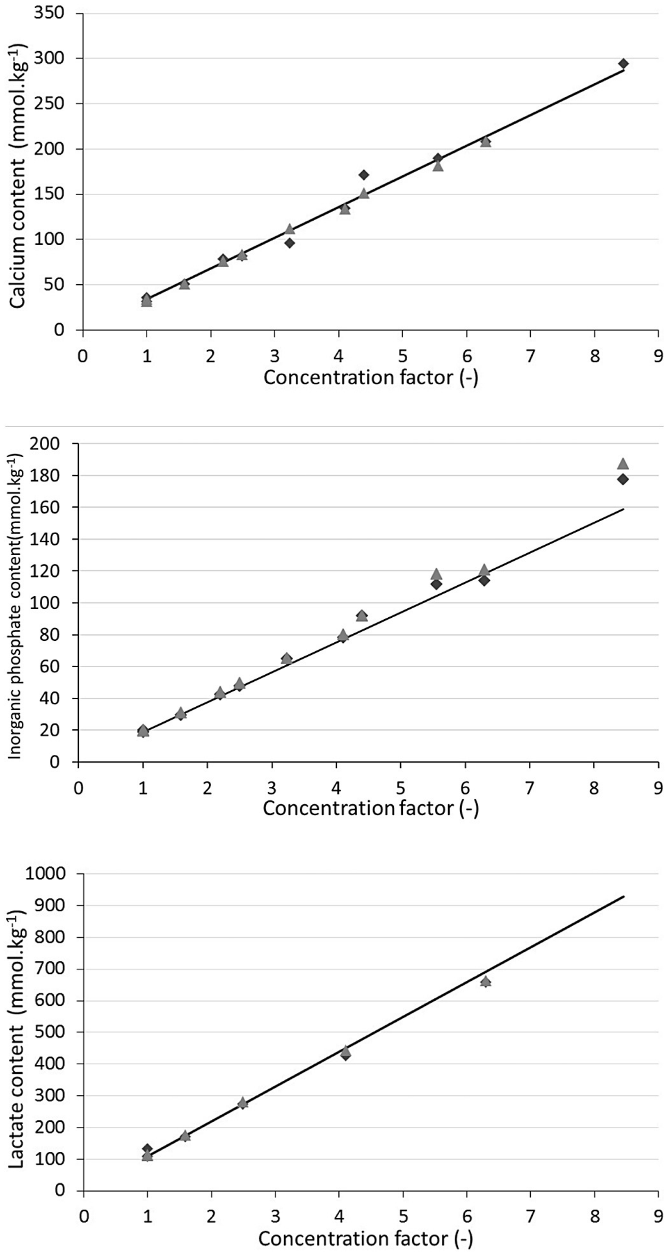

Fig. 7. Evolution of the calcium, inorganic phosphate and lactate contents as a function of the concentration factor during vacuum evaporation of LAW. The symbols ◆ and ▲ correspond to the total and soluble experimental contents, respectively. The experimental contents are compared to the calculated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

the evolution of calcium ions, the total citrate content increased linearly with the concentration factor up to $HAW_{2.5}$, after 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, 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 made during the experiments, i.e., the presence of a brittle, white deposit on the inner surface of the evaporation tubes, characteristic of a mineral deposit (Morison & Thorpe, 2002).

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 the evaporator and the precipitation of both ions in the concentrate for concentration factors over 2.5. Inorganic phosphate ions were not involved in the formation of the deposit and the precipitate. These results can be explained in terms of the pH of the concentrates and the association constants of the ionic forms present. The values for the association constants of the salt equilibria given by Holt, Dalgleish, and Jenness (1981) provide partial indications about the 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 was about 60 °C. Moreover and as already mentioned, the concentration factor influenced the ionic strength and the ionic activity coefficients. Finally, equilibrium conditions were not reached in the evaporator (Jeurnink & Brinkman, 1994).

The pH of the concentrates beyond $HAW_{2.5}$ was 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:

$$Ca^{2+} + H_2PO_4^- \rightleftarrows CaHPO_4 + H^+ \quad (1)$$

$$Ca^{2+} + H_2Cit^- \rightleftarrows (CaHCit)_{aq} + H^+ \quad (2)$$

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.

$$Ca^{2+} + HCit^{2-} \rightleftarrows (CaHCit)_{aq} \tag{3}$$

where $CaHPO_4$ 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:

$$(CaHCit)_{aq} \rightleftarrows Ca_3Cit_2 \tag{4}$$

The solubility of calcium citrate is also considered as low. Vavrusova and Skibsted (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 $HCit^{2-}$ ($Ka = 876\,M^{-1}$) 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 Ca_3Cit_2 (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).

3.6.2. LAW

During LAW concentration, the total calcium, inorganic phosphate and lactate contents 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 LAW, in agreement with the visual observation of the evaporation tubes after experiments. In the same way, diffusible calcium, inorganic phosphate and lactate contents were similar to total experimental contents. They increased linearly with the concentration factor, confirming, as shown in Fig. 2, that no precipitation of minerals occurred over the entire range of concentration factors studied.

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, $H_2PO_4^-$ and $Lact^-$, respectively. Calcium may then react with both ions according to the following reactions:

$$Ca^{2+} + H_2PO_4^- \rightleftarrows CaHPO_4 + H^+ \tag{5}$$

$$Ca^{2+} + Lact^- \rightleftarrows (CaLact_2)_{aq} \tag{6}$$

where $CaHPO_4$ is a poorly soluble salt and $(CaLact_2)_{aq}$ is a soluble complex ion. When saturation conditions are reached, $(CaLact_2)_{aq}$ would precipitate according to the reaction:

$$(CaLact_2)_{aq} \rightleftarrows CaLact_2 \tag{7}$$

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 $CaLact_2$/100 g of water at 24 °C) (Kubantseva, Hartel, & Swearingen, 2004), and the threshold concentration of reaction (7) was not exceeded here, as shown by the absence of the precipitate in the concentrated LAW (Fig. 2).

3.7. Sodium, potassium, chloride and magnesium contents

Monovalent ions (sodium, potassium, chloride) and divalent magnesium contents were also determined in the different concentrates and their respective diffusible phases (Table 2 for HAW and Table 3 for LAW). There was some discrepancy in the experimental results for the LAW concentration trials. As an example, the mineral composition in the diffusible phase of the more concentrated product ($LAW_{8.5}$) could not be determined due to the small quantity of 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 with the concentration factor. This suggests that these ions were not insoluble in HAW and LAW concentrates.

4. Conclusions

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

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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