Insolubilisation of mineral salts during vacuum concentration of dairy ultrafiltration permeates in relation to fouling of evaporators

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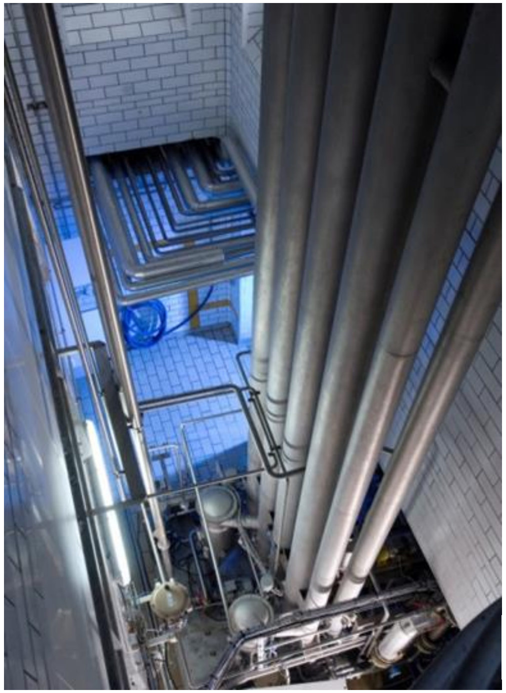
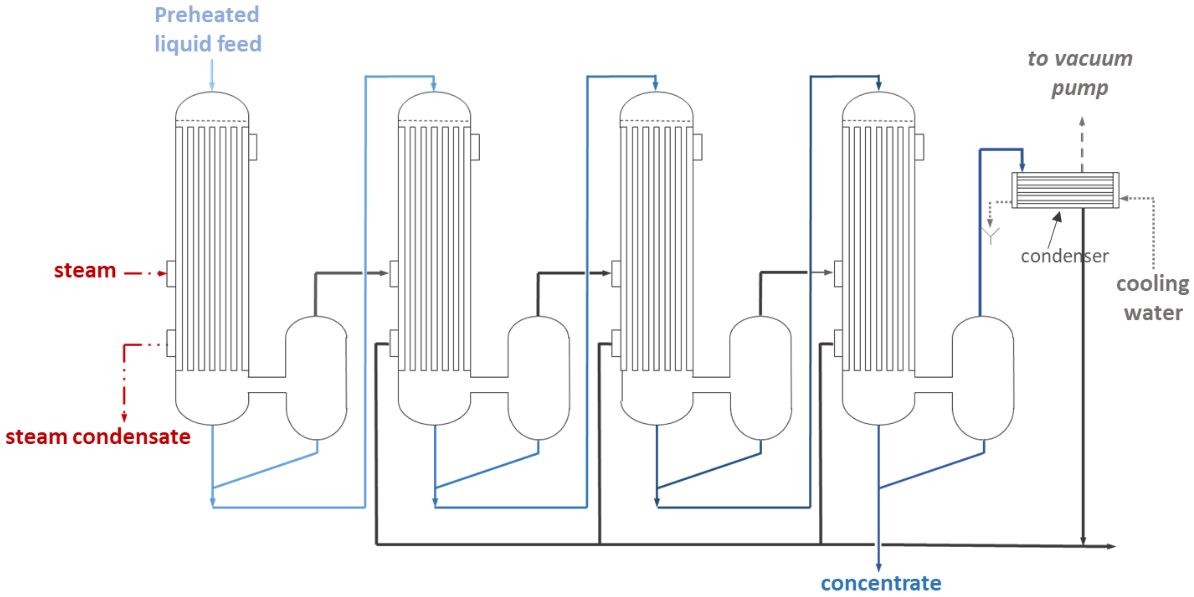
Vacuum evaporation of dairy products

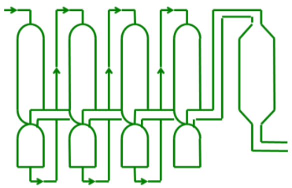




Falling-film evaporator # latent heat exchanger

DM=dry matter content (g.kg[-1])

Fouling of evaporators vs heat-exchangers



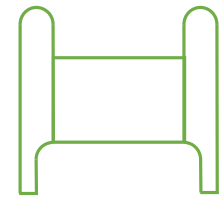
Falling-film evaporators

Temperature

Different operating conditions between both equipements

Residence time

Concentration



Heat-exchangers

Fouling mechanisms and deposit composition might be different between heat-exchangers and falling-film evaporators

(Jeurnink and Brinkman, 1994; Morison, 2015)

% in deposit (per ton of treated product)	Whey 28% DM	
	Heat-exchanger (70°C, 90 s)	Evaporator 28 → 55% DM
Proteins	**19**	**8**
Calcium	24	18
Phosphate	**30**	**3**
Citrate	**24**	**62**

− proteins

− phosphate

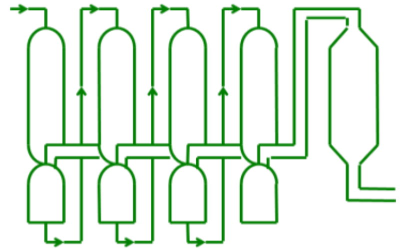
+ citrate

(Jeurnink and Brinkman, 1994)

Fouling of evaporators during whey concentration

whey

Main origin:
cheese manufacture
Acid precipitation of casein



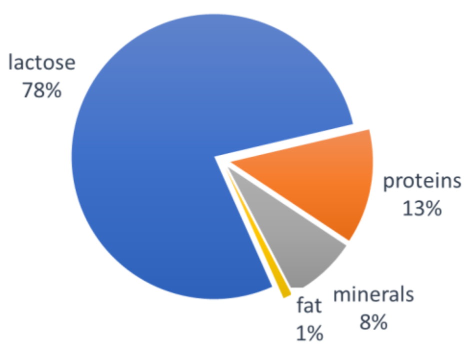
in some cases

fouling of inner surfaces of tubes

Rough composition … but highly variable !

Dry matter content of whey: about 60 g.kg^{-1}

Composition of dry matter (sweet whey)

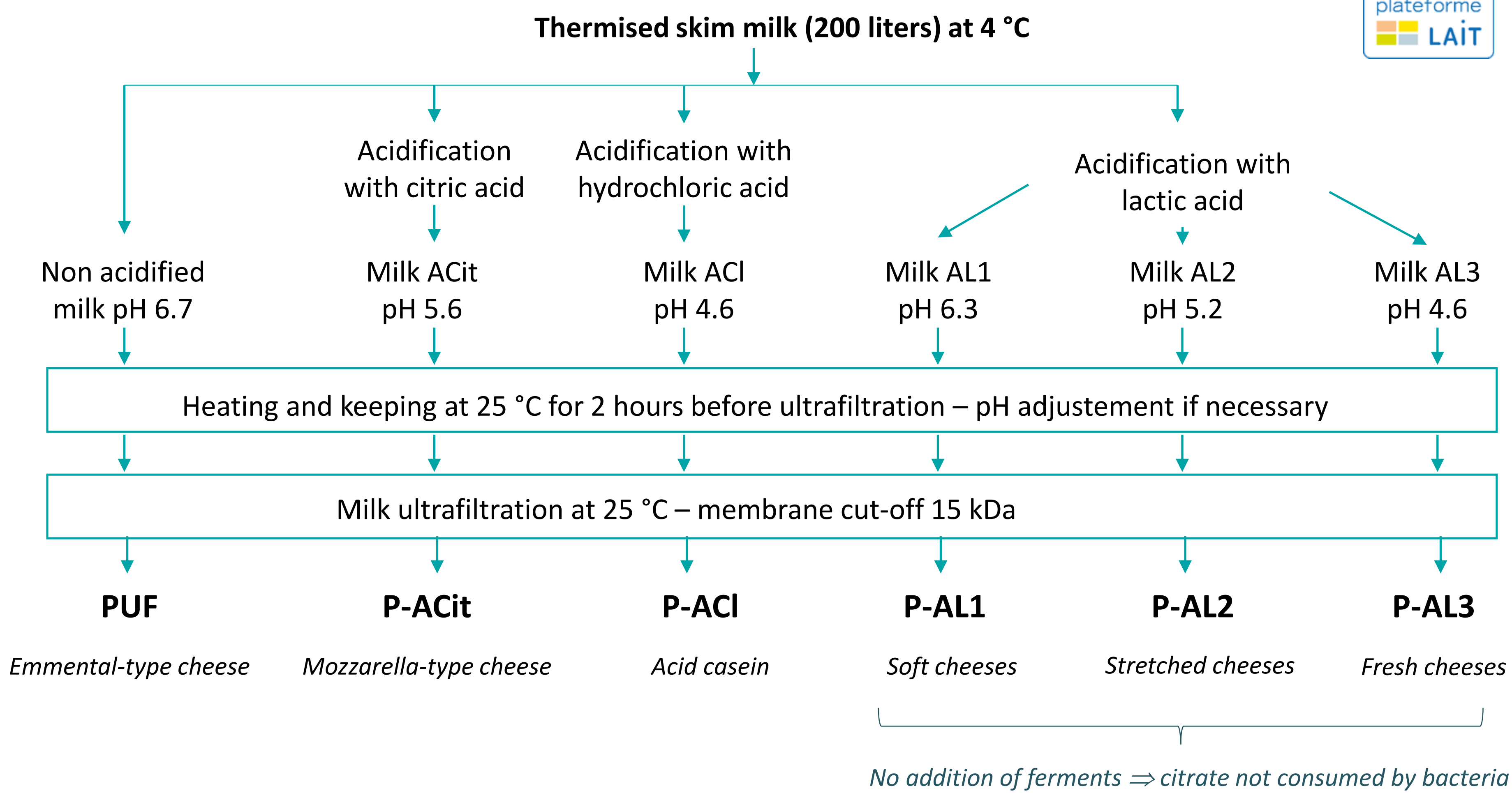


*How **mineral composition** and **initial pH of whey** influence the nature and the quantity of precipitate formed during concentration?*

Predict the behaviour of the mineral fraction during whey concentration

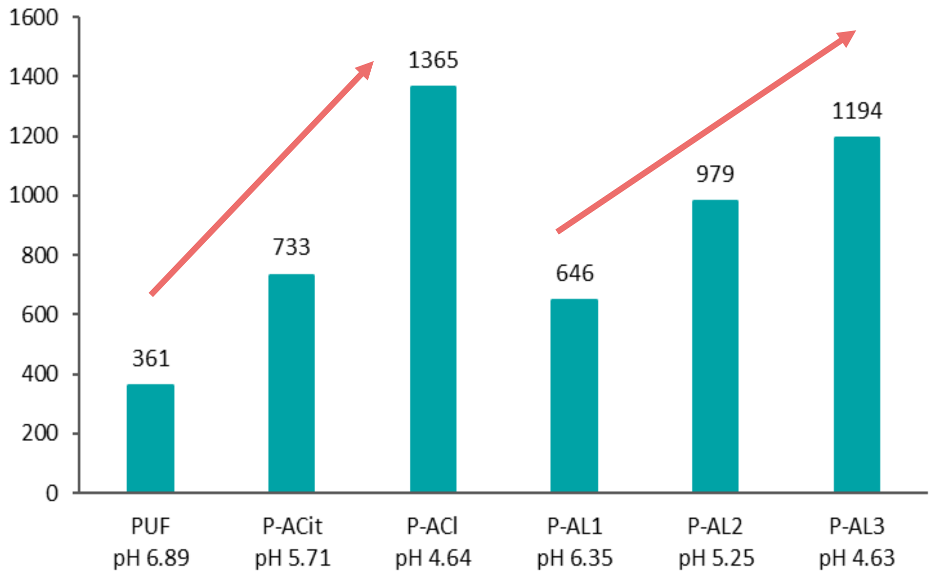
Concentration of **model ultrafiltration permeates** (UFP)

Preparation of model ultrafiltration permeates

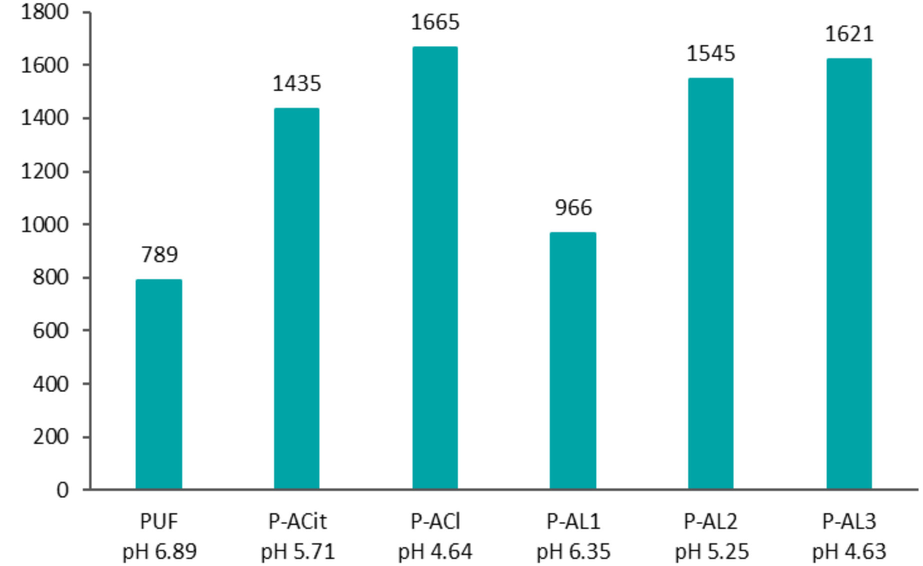


Mineral composition of initial UF permeates

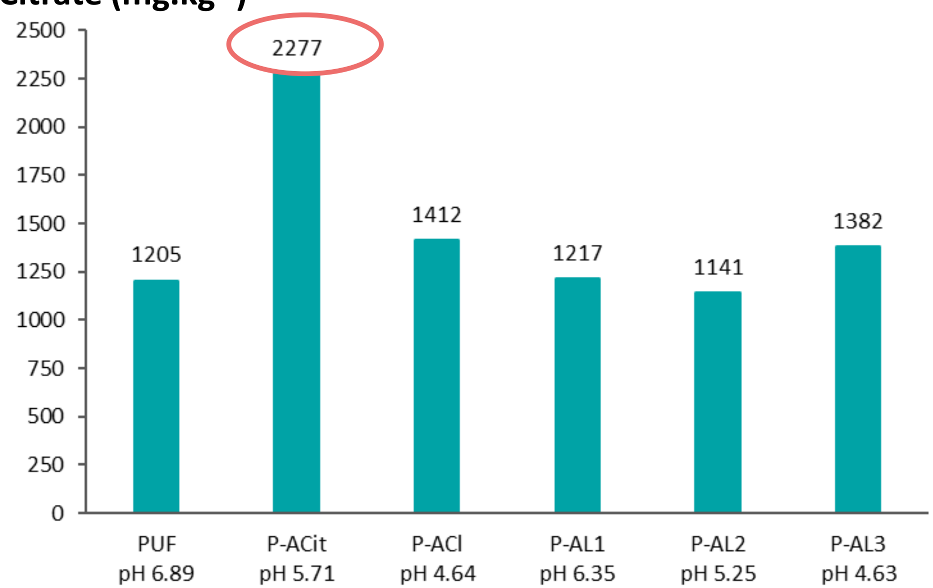
Calcium (mg.kg^{-1})

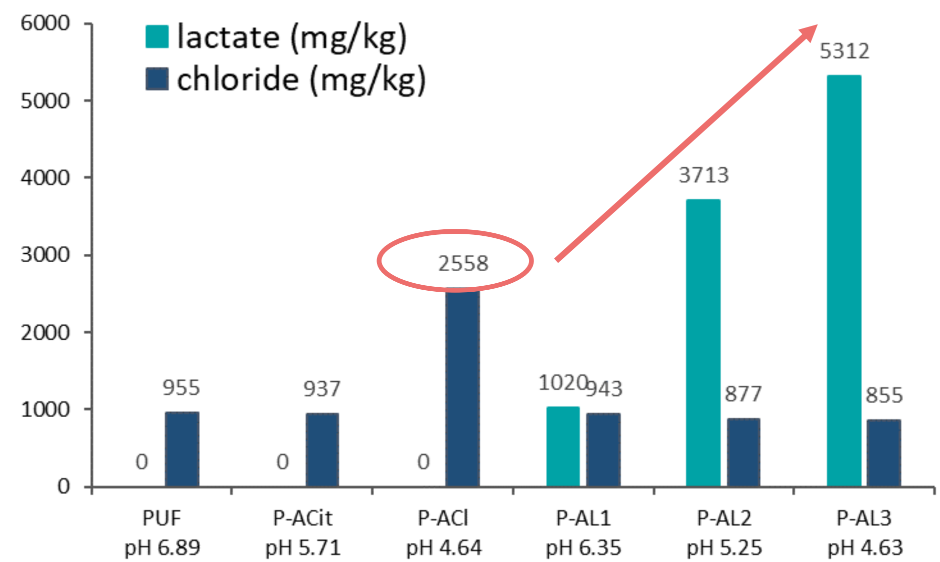


Phosphate (mg.kg^{-1})



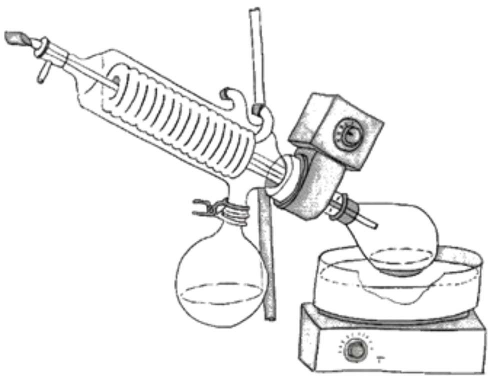
Citrate (mg.kg^{-1})





Concentration and characterization of concentrates

Evaporation T°C=46-56 °C



Target values for concentration factor (CF)	*Duration of concentration*
CF 3	≈20 min
CF 5	
CF 7	
CF 9	≈ 4 hours

2 series of experiments: set #1 and set #2

- ✓ pH
- ✓ Dry matter content (DM)
- ✓ Ash content
- ✓ Protein content
- ✓ Anions and cation contents (total and soluble)

Insoluble ion content ⇒ difference between total and soluble contents

Centrifugation of the most concentrated permeates ⇨ *Analysis of supernatants*

Estimation of the composition of the precipitates from the composition of concentrates and supernatants

Experimental vs theoretical results

Milk Salt GLM software®

Prediction of ion distribution in dairy liquids - f(pH, ion contents)

Presented results :

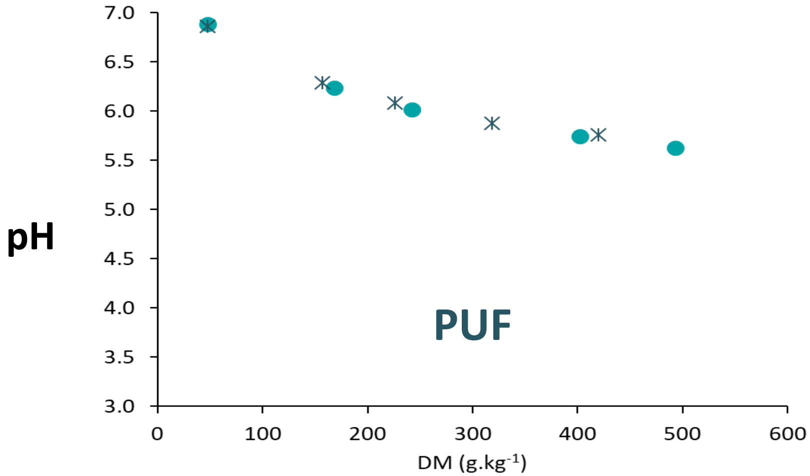
PUF | P-ACit | P-AL1 | P-AL3

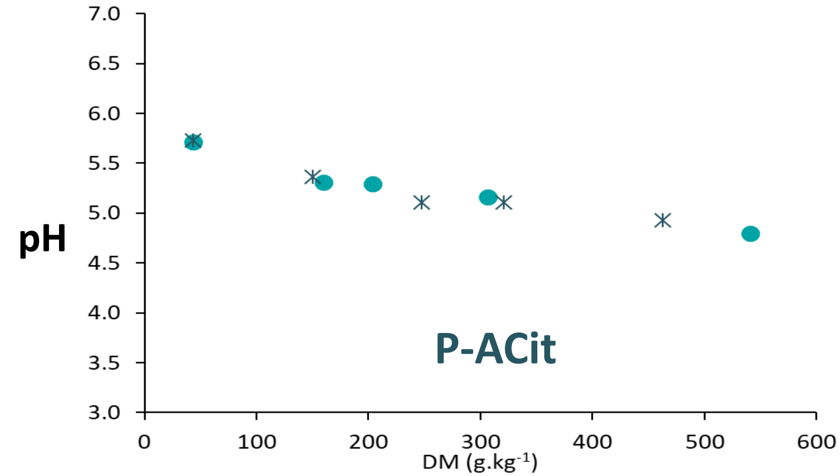
Calcium | Inorganic phosphate | Lactate | Citrate

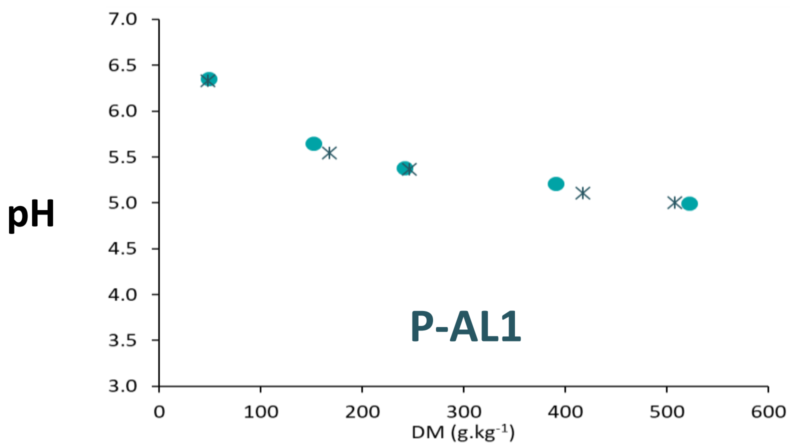
Solubility of calcium salts

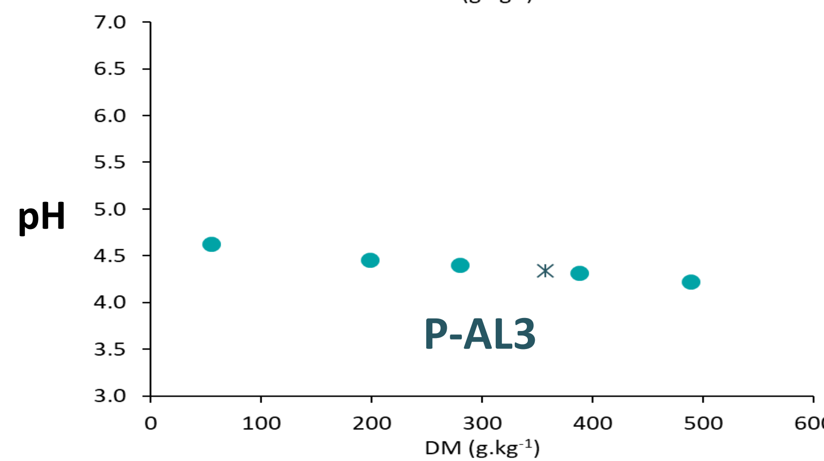
$CaHPO_4$	0.6 mM (milk, 25°C)
Ca_3Cit_2	1.48 mM (water, 25°C)
$CaLact_2$	280 mM (water, 25°C)

pH evolution during UF permeate concentration









- Precipitation of calcium phosphate salt with concomitant release of H^+

  $Ca^{2+} + HPO_4^{2-} \longrightarrow CaHPO_4$

  $H_2PO_4^- \longrightarrow HPO_4^{2-} + H^+$

- Precipitation of other salts (calcium citrate)
- Increase of ionic strength due to concentration → decreasing activity coefficients

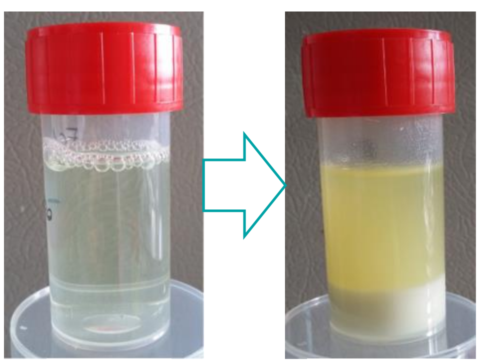
Impact on the anionic forms in the concentrates and their affinity for calcium

Ion composition of the precipitates

Composition deduced from the composition of the most concentrated permeates and their corresponding supernatants after centrifugation

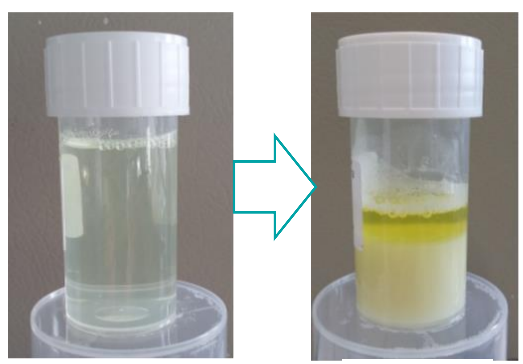
in 100 g of concentrate	PUF CF 8.9	P-Acit CF 10.7	P-AL1 CF 10.6
Lactose (g)	*100.2*	*87.2*	*96.7*
Calcium (mmol)	52	150	17
Inorganic PO_4 (mmol)	26	5	13
Citrate (mmol)	3	88	3
Lactate (mmol)	0	0	2

PUF



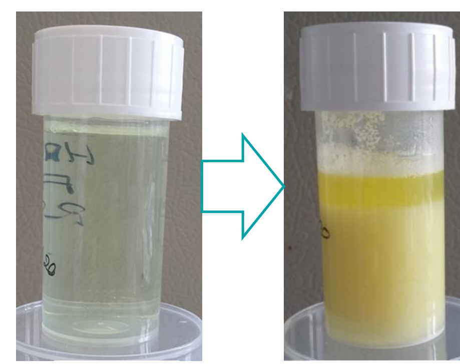
CF 1 CF 8.9

P-ACit



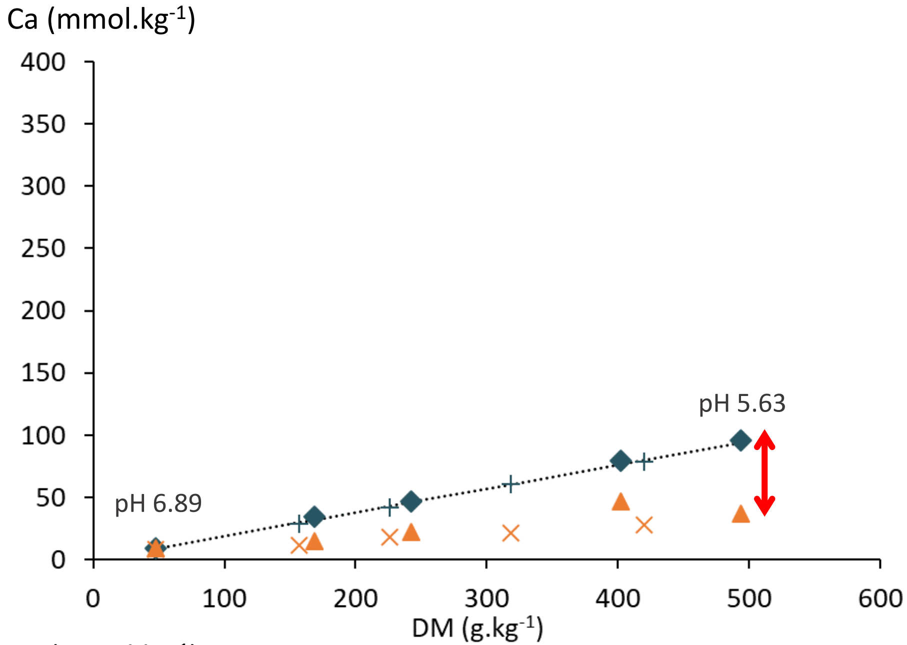
CF 1 CF 10.7

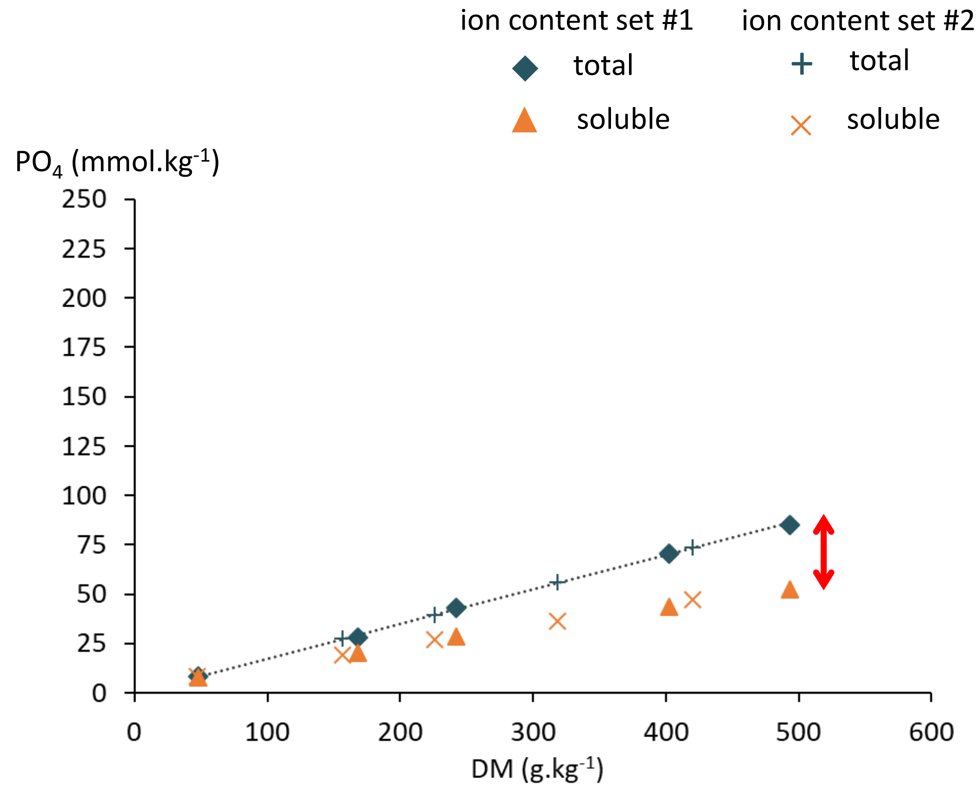
P-AL1

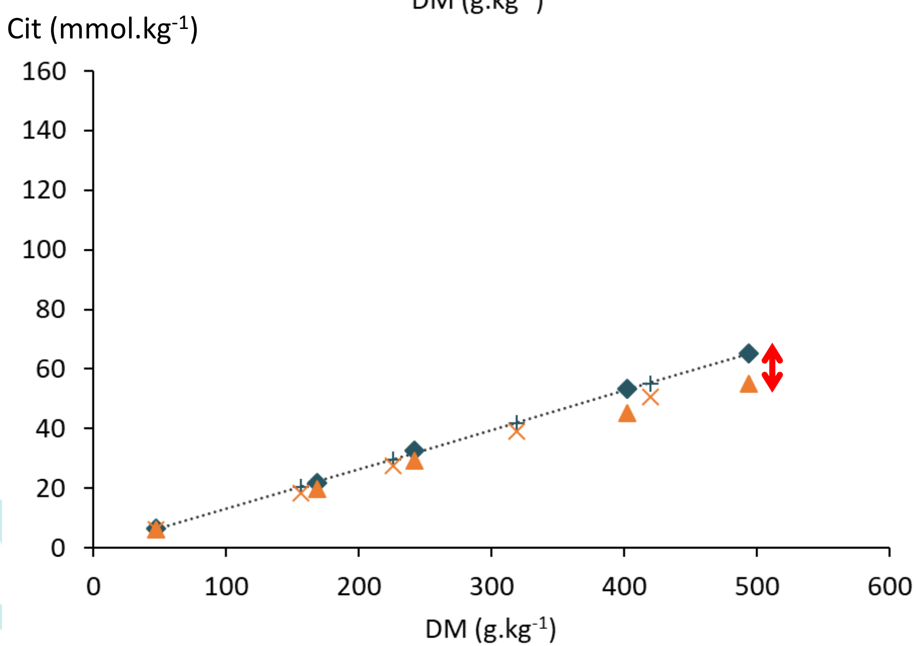


CF 1 CF 10.6

PUF concentration







- Calcium phosphate at the edge of the precipitation in PUF at pH 6.6-6.7
- Phosphate ion (HPO_4^{2-}) > free citrate ion

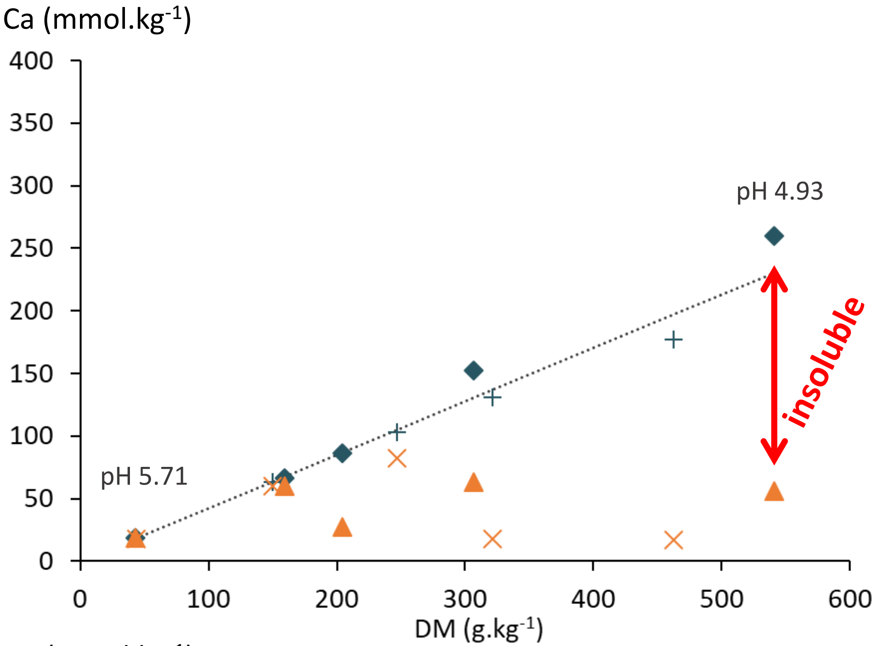
During concentration and with decreasing pH,

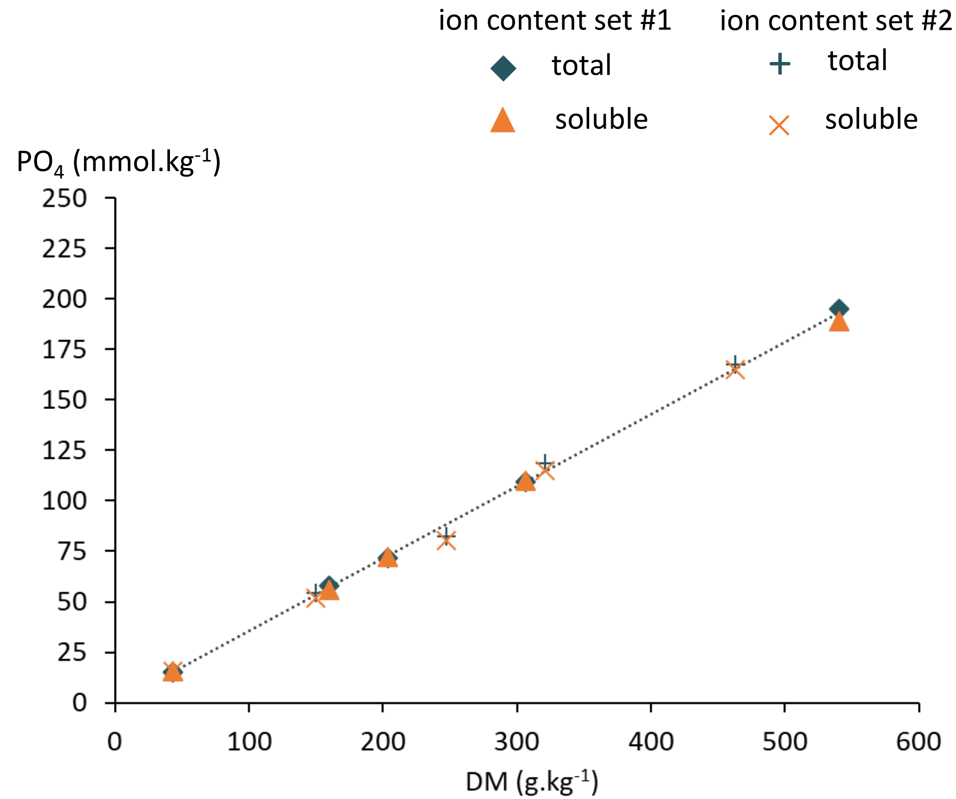
1. slow co-precipitation of calcium citrate
2. progressive solubilisation of calcium phosphate salt initially formed

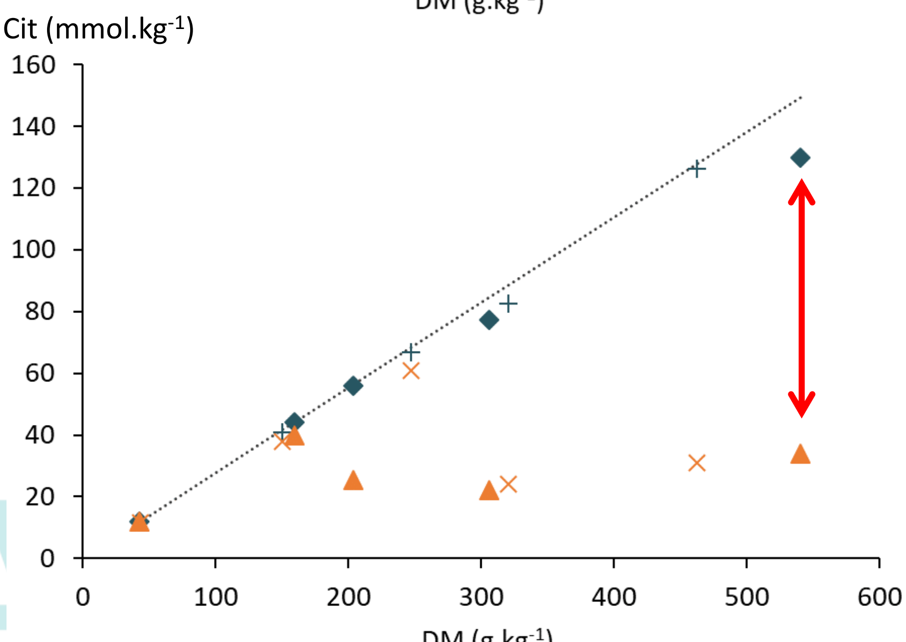
Experiment: Ca & PO_4 precipitated = 62 and 38 mM

: Ca & PO_4 precipitated = 62 and 34 mM

P-ACit concentration



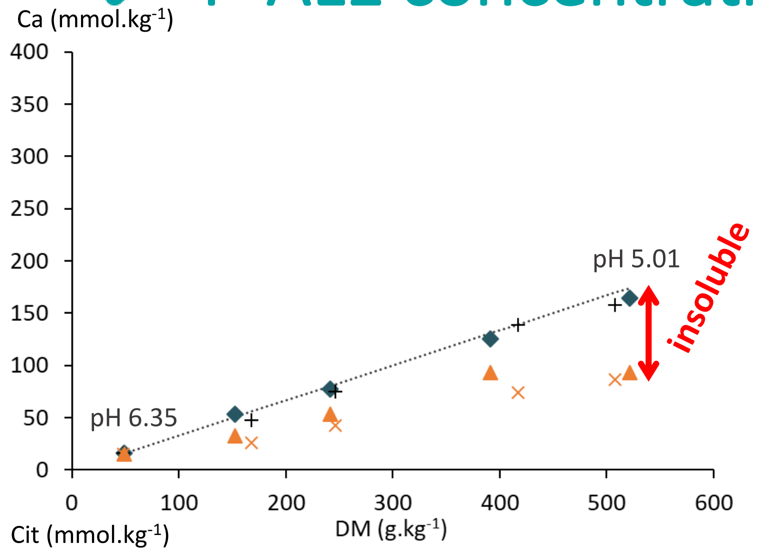


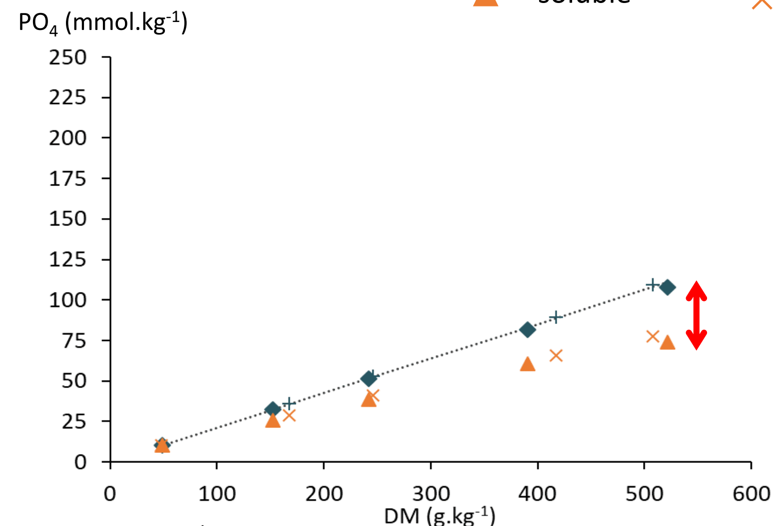


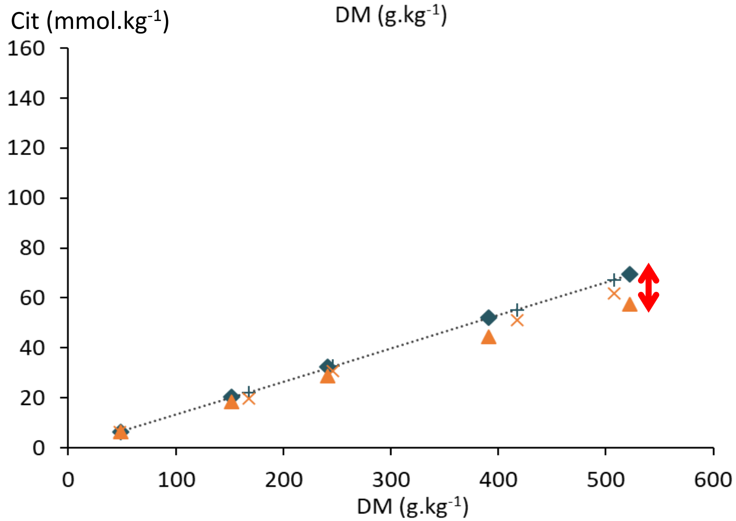
- Higher contents of Ca, PO_4 and Citrate
- Strong chelating capacity of citrate with calcium ($CaCit^-$ or CaHCit complex)

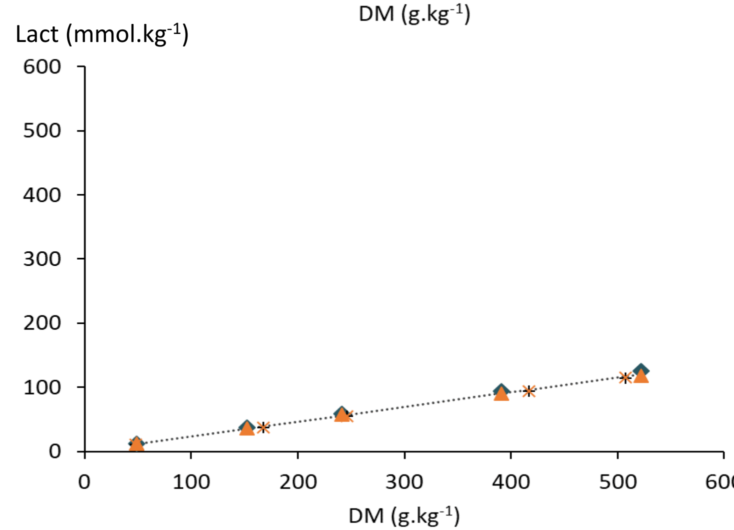
- Supersaturation of citrate and calcium ions / solubility limit exceeded ⇒ **precipitation**
- Strong chelating capacity of citrate ⇒ less ionic calcium available for calcium phosphate association

P-AL1 concentration







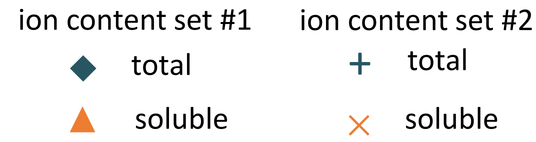


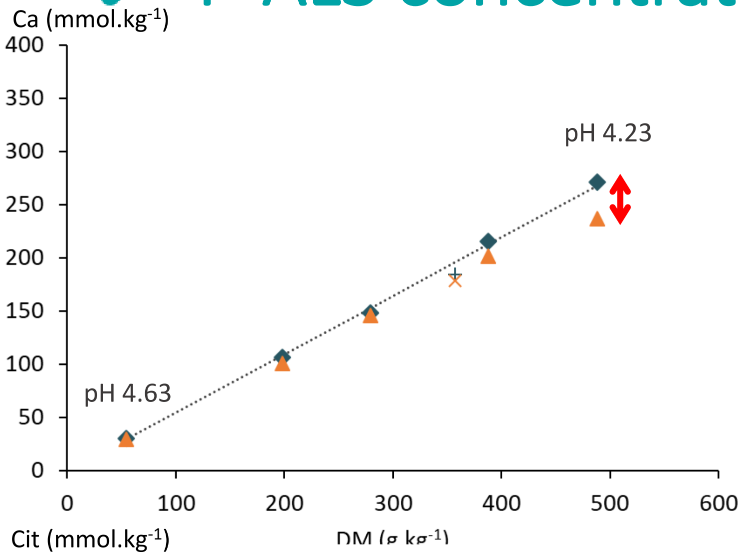
- Situation quite similar to PUF concentration
- Phosphate ion under the form HPO_4^{2-}
- Free lactate ion (little affinity to calcium)

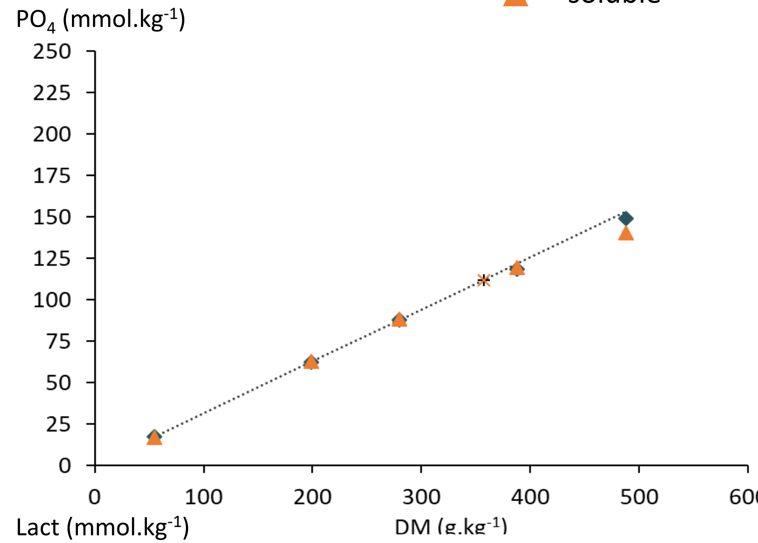
Experiment: Ca & PO_4 precipitated = 95 and 52 mM

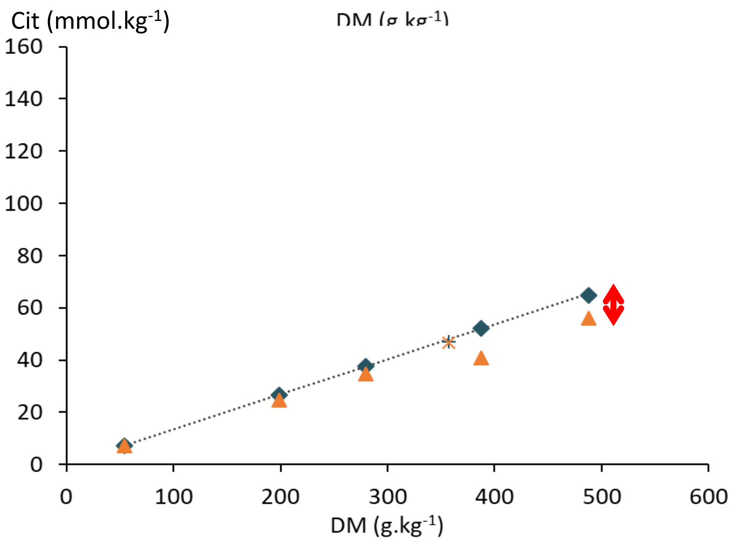
MilkSaltsGLM : Ca & PO_4 precipitated = 93 and 51 mM

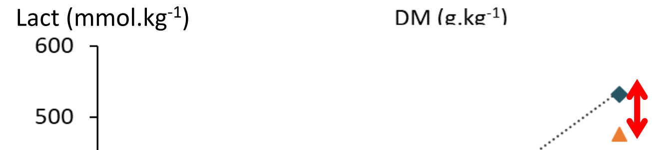
P-AL3 concentration











- high lactate content + resulting formation of $CaLact^-$ complex ⇒ less ionic calcium available for potential association with citrate and phosphate
- High solubility of calcium lactate salt
- Low citrate content + low affinity of the ionic form of phosphate ($H_2PO_4^-$) with calcium

Lactate ions displaced the equilibrium in the calcium-phosphate-citrate system

Calcium distribution in initial P-AL3:

Free Ca (50%) CaLact (23%)

$CaCit^-$ (9.4 %)

$CaHCit^-$ (5.8 %) $CaCl_2$ (4.7 %) CaH_2PO_4 (5.9 %)

Conclusions

Concentration of dairy ultrafiltration permeates having different mineral composition and initial pH

Depending of the type of permeates (nature and quantities of ion species) and pH, either precipitation of calcium salts or little ion precipitation

- **Calcium phosphate** → dominant mineral specie in the precipitate if phosphate ion under the ionic form HPO_4^{2-}
- **At lower pH, calcium citrate precipitation is favoured** (if citrate ion in sufficient amounts) → strong chelating effect of citrate ion with calcium + less affinity of ionic form of phosphate with calcium
- **in presence of high quantity of Lactate** → lactate ion associated with calcium and **less ionic calcium available for citrate and phosphate ions** / inhibition of calcium citrate and calcium phosphate precipitations (but effect of lactate ion on lactose crystallization)

Next steps

- Contribution of proteins
- Mechanisms involved

Recovery of deposits ? → Development of a milli- and/or microfluidic system

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Thank you for your attention !