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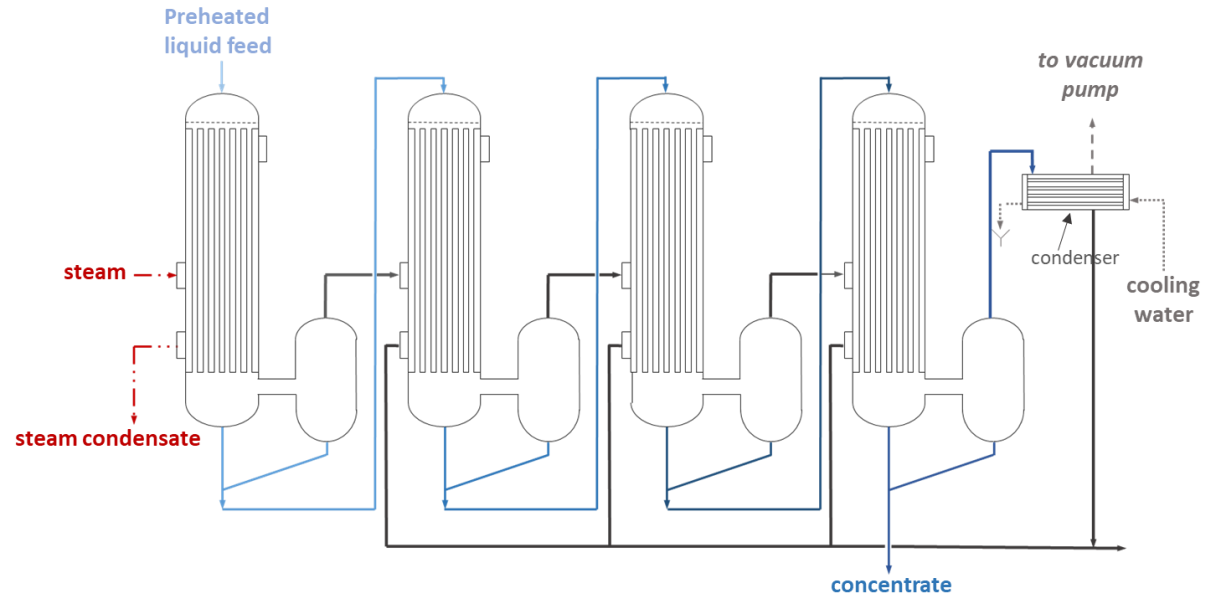
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## ➤ Insolubilisation of mineral salts during vacuum concentration of dairy ultrafiltration permeates in relation to fouling of evaporators

Gaëlle Tanguy, Eric Beaucher, Anne Dolivet, Ali Kerjough,  
Marie-Bernadette Maillard, Pascaline Hamon, Thomas Croguennec

*UMR Science and Technology of Milk and Eggs – Rennes (France)*

# ➤ Vacuum evaporation of dairy products



**Falling-film evaporator # latent heat exchanger**

70 °C

temperature

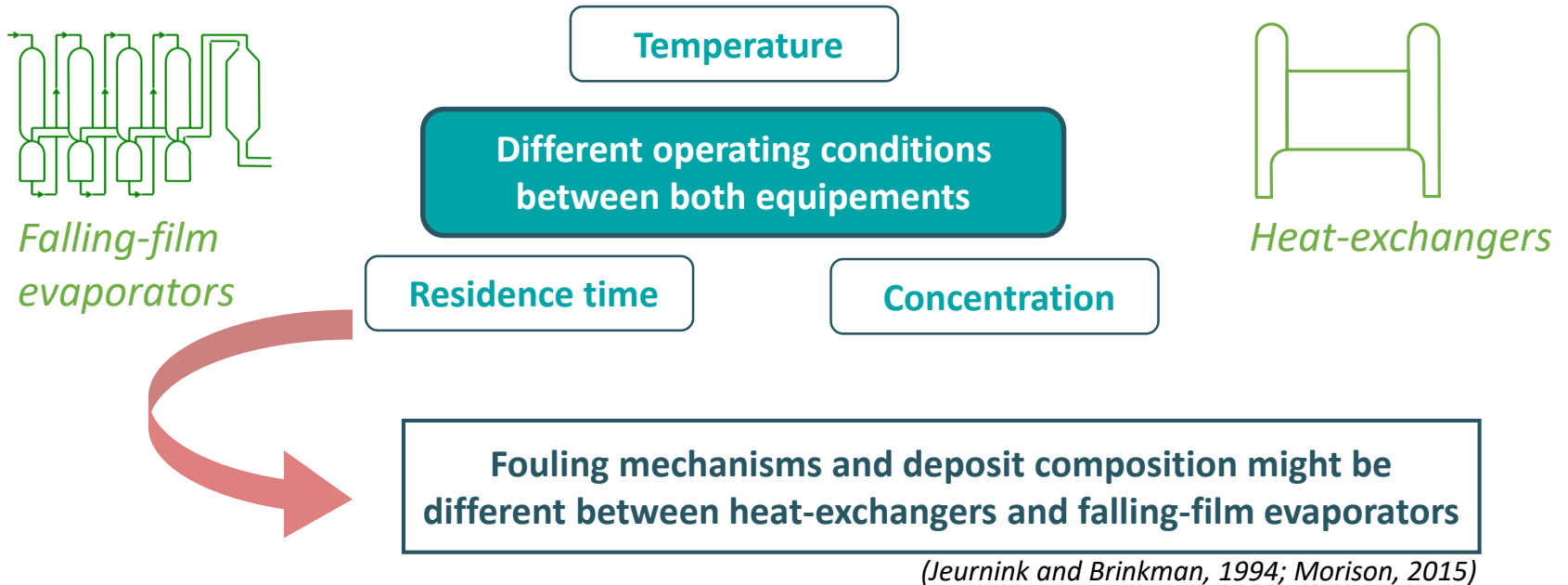
45 °C

Residence time 10 to 20 minutes

% DM

% DM

# ➤ Fouling of evaporators vs heat-exchangers



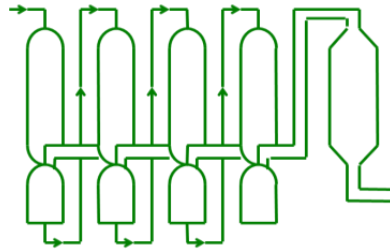
% in deposit (per ton of treated product)	Whey 28% DM		
	Heat-exchanger (70°C, 90 s)	Evaporator 28 → 55% DM	
Proteins	19	8	■ proteins
Calcium	24	18	
Phosphate	30	3	■ phosphate
Citrate	24	62	⊕ citrate

*(Jeurnink and Brinkman, 1994)*

# ➤ Fouling of evaporators during whey concentration



whey



*in some cases*



*fouling of inner surfaces of tubes*



Main origin:  
cheese manufacture  
Acid precipitation of casein

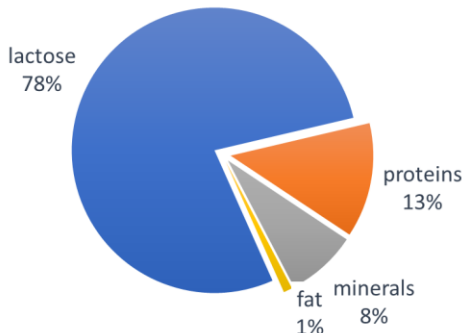
***How mineral composition and initial pH of whey influence the nature and the quantity of precipitate formed during concentration?***

Rough composition ... but highly variable !

Dry matter content of whey: about 60 g.kg<sup>-1</sup>

***Predict the behaviour of the mineral fraction during whey concentration***

Composition of dry matter (sweet whey)

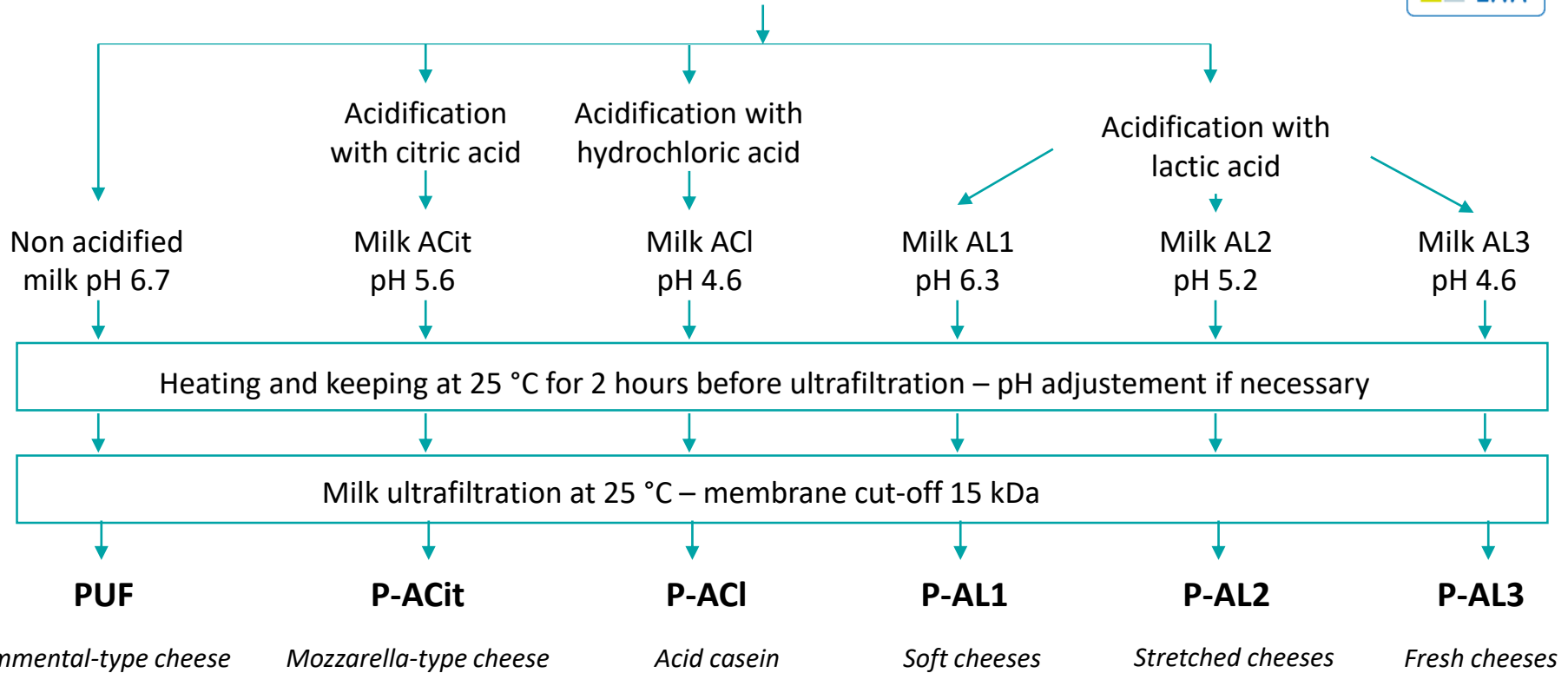


Concentration of **model ultrafiltration permeates (UFP)**

# ➤ Preparation of model ultrafiltration permeates



Thermised skim milk (200 liters) at 4 °C

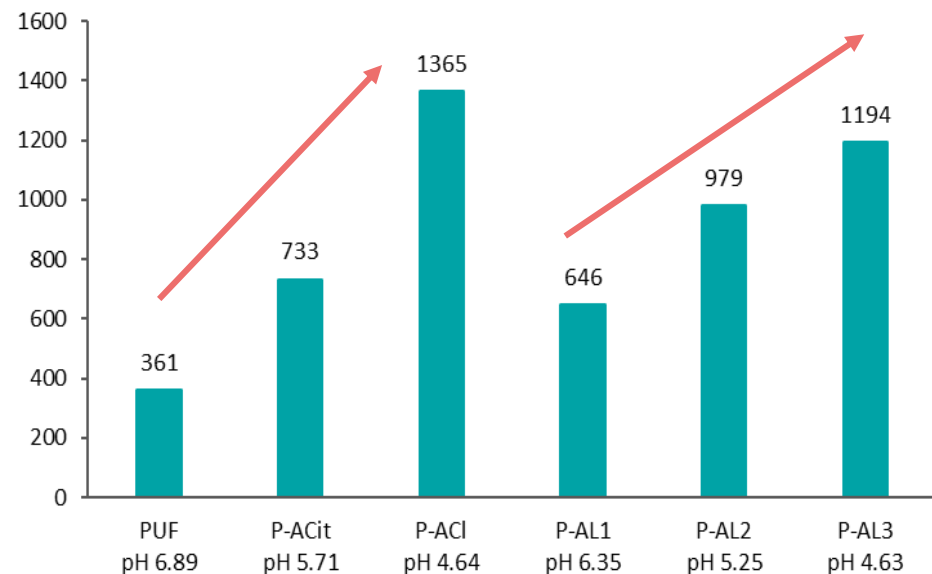


No addition of ferments ⇒ citrate not consumed by bacteria

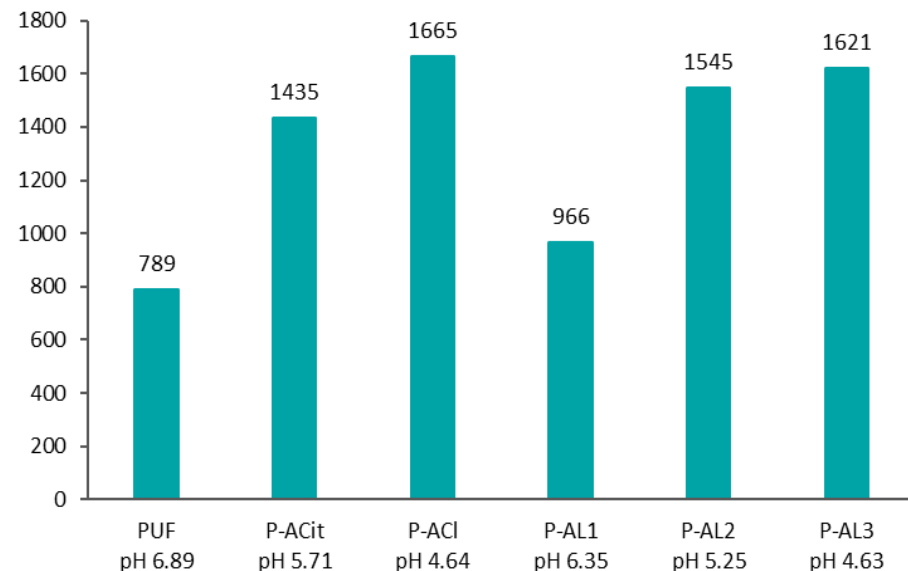


# ➤ Mineral composition of initial UF permeates

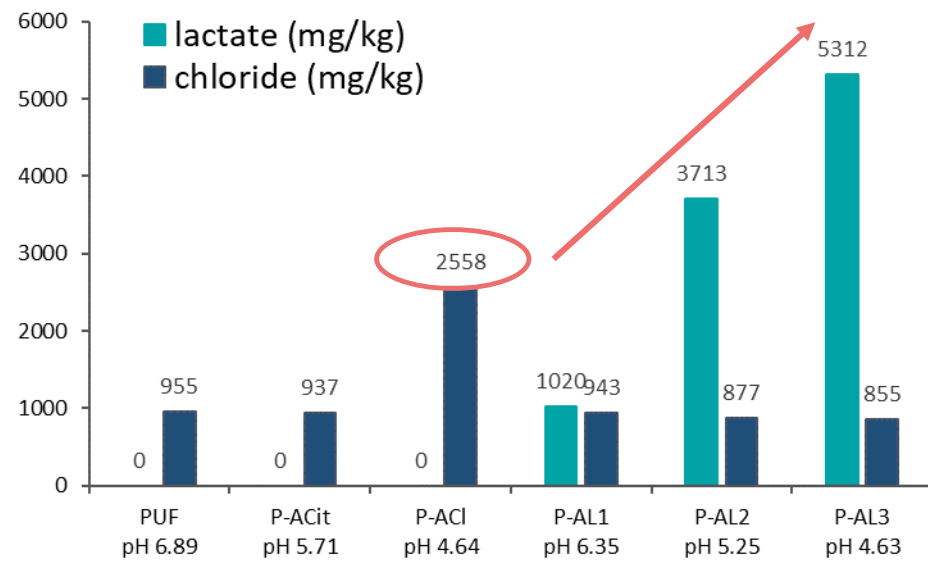
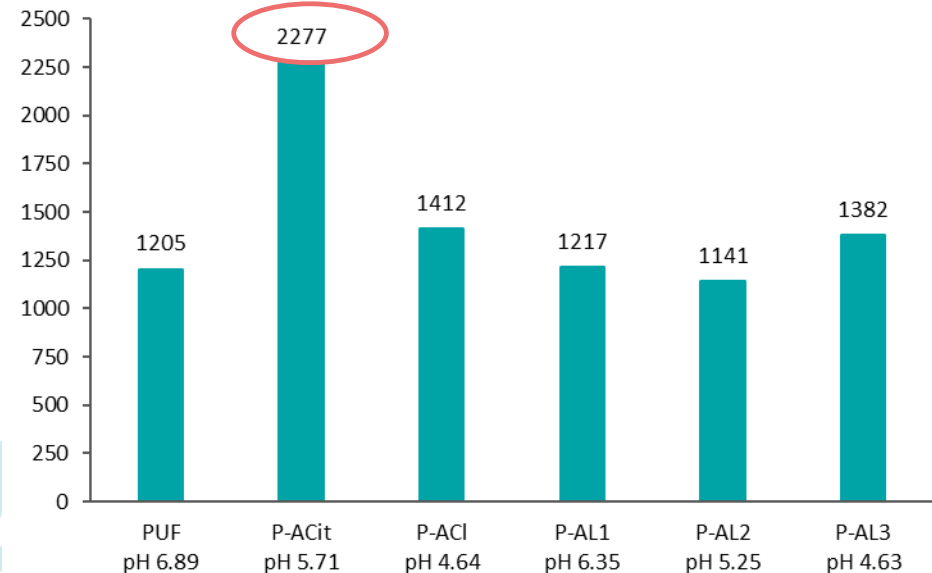
## Calcium (mg.kg<sup>-1</sup>)



## Phosphate (mg.kg<sup>-1</sup>)

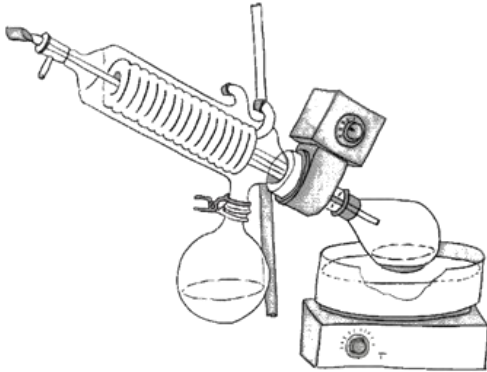


## Citrate (mg.kg<sup>-1</sup>)



# ➤ Concentration and characterization of concentrates

Evaporation  $T^{\circ}\text{C}=46-56^{\circ}\text{C}$



Target values for concentration factor (CF)

- CF 3
- CF 5
- CF 7
- CF 9

Duration of concentration

≈ 20 min

≈ 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 -  $f(\text{pH}, \text{ion contents})$

Presented results :

PUF

P-ACit

Calcium

Inorganic phosphate

P-AL1

P-AL3

Lactate

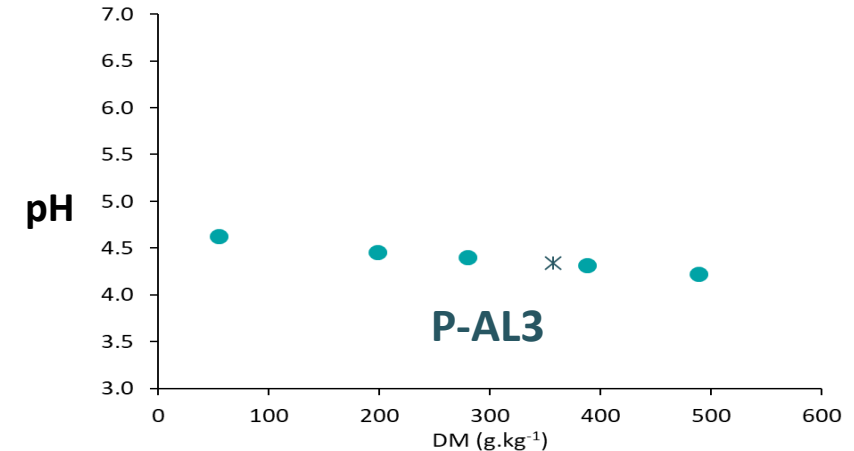
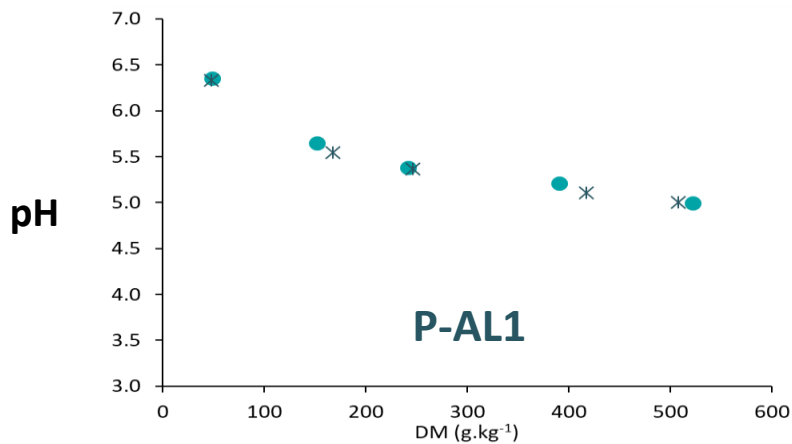
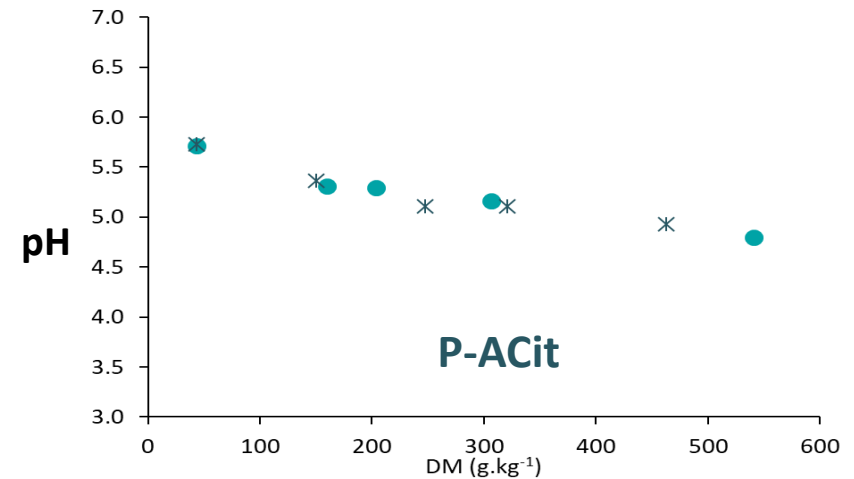
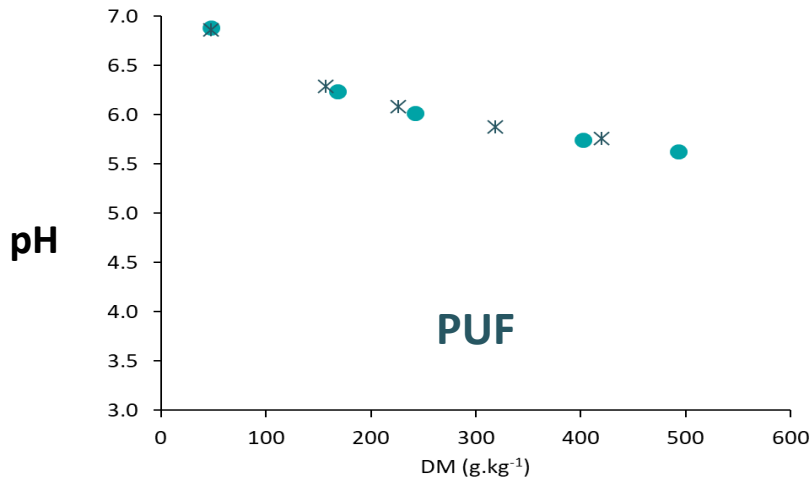
Citrate

Solubility of calcium salts

$\text{CaHPO}_4$	0.6 mM (milk, 25°C)
$\text{Ca}_3\text{Cit}_2$	1.48 mM (water, 25°C)
$\text{CaLact}_2$	280 mM (water, 25°C)



# ➤ pH evolution during UF permeate concentration



- Precipitation of calcium phosphate salt with concomitant release of H<sup>+</sup>



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

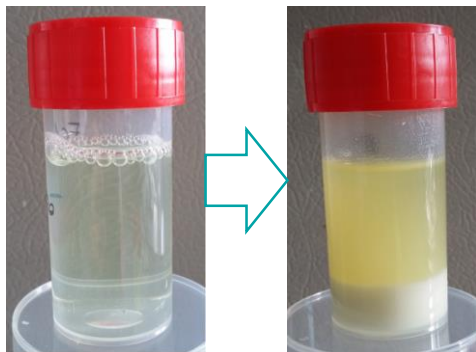
**Impact on the anionic forms in the concentrates and their affinity for calcium**

# ➤ 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
<i>Lactose (g)</i>	100.2	87.2	96.7
<b>Calcium (mmol)</b>	52	150	17
<b>Inorganic PO<sub>4</sub> (mmol)</b>	26	5	13
<b>Citrate (mmol)</b>	3	88	3
<b>Lactate (mmol)</b>	0	0	2

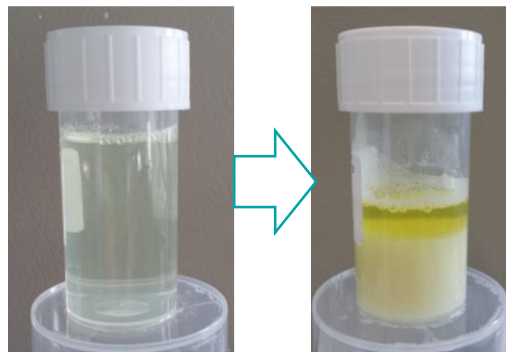
**PUF**



CF 1

CF 8.9

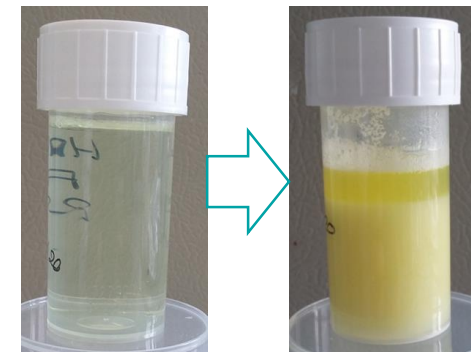
**P-ACit**



CF 1

CF 10.7

**P-AL1**



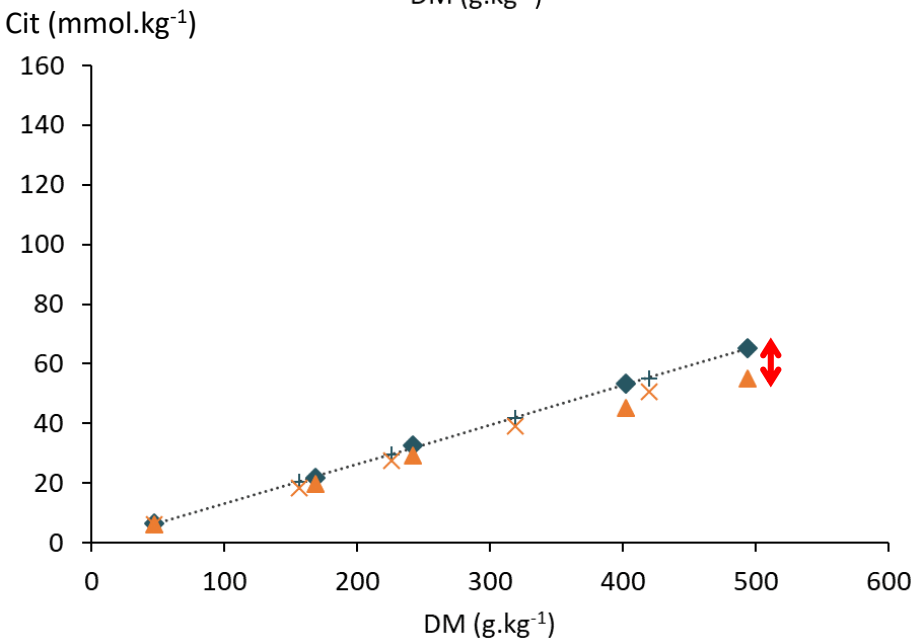
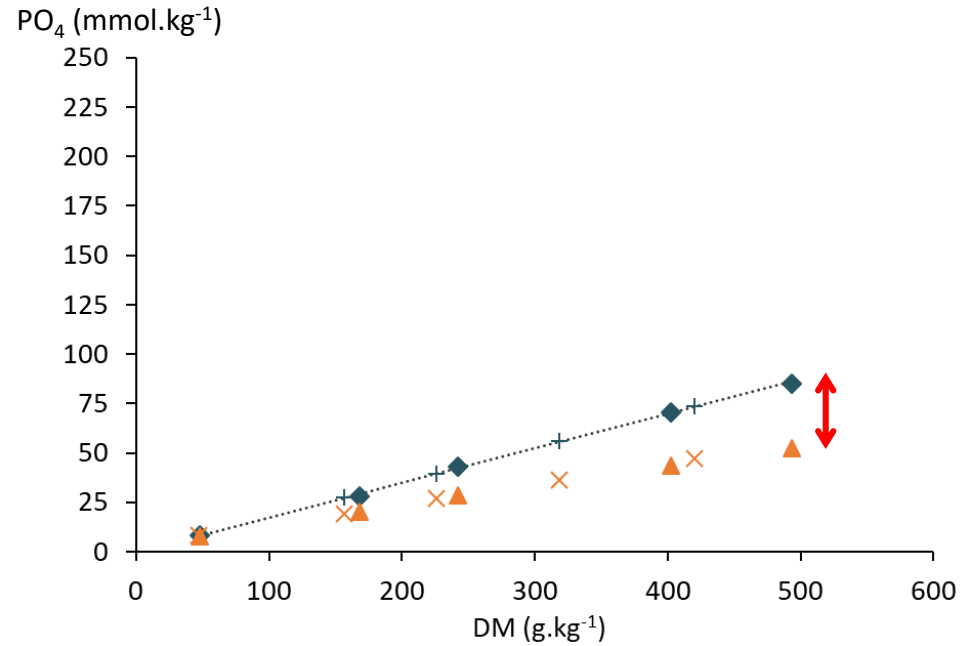
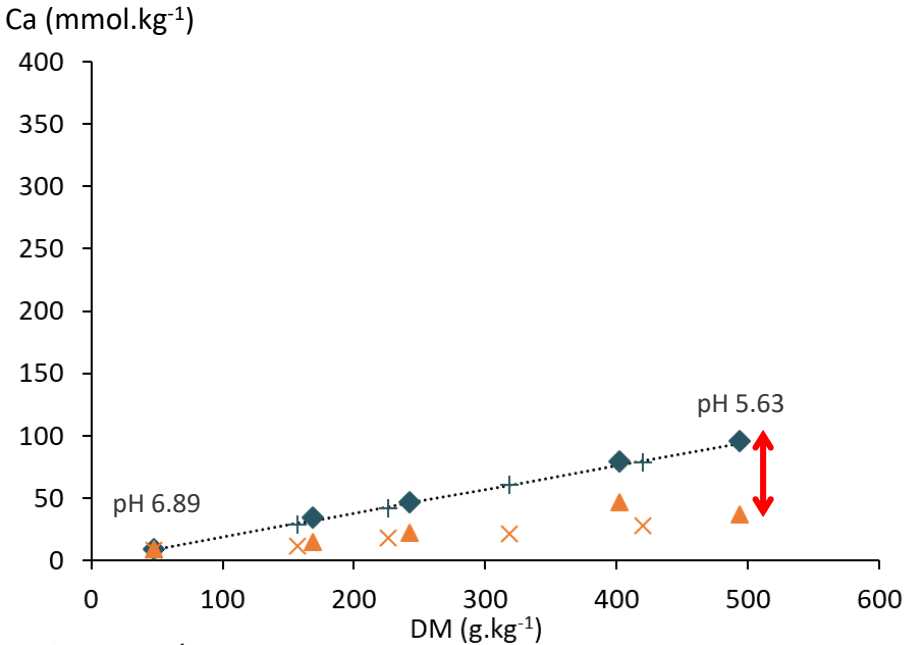
CF 1

CF 10.6

# ➤ PUF concentration

ion content set #1  
 ◆ total  
 ▲ soluble

ion content set #2  
 + total  
 × soluble



- Calcium phosphate at the edge of the precipitation in PUF at pH 6.6-6.7
- Phosphate ion ( $\text{HPO}_4^{2-}$ ) > 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

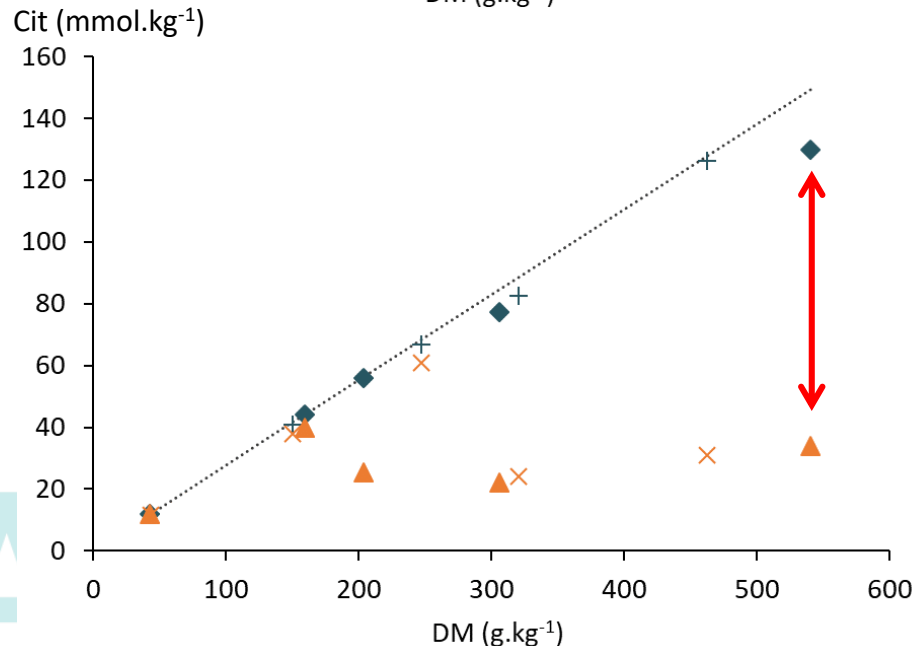
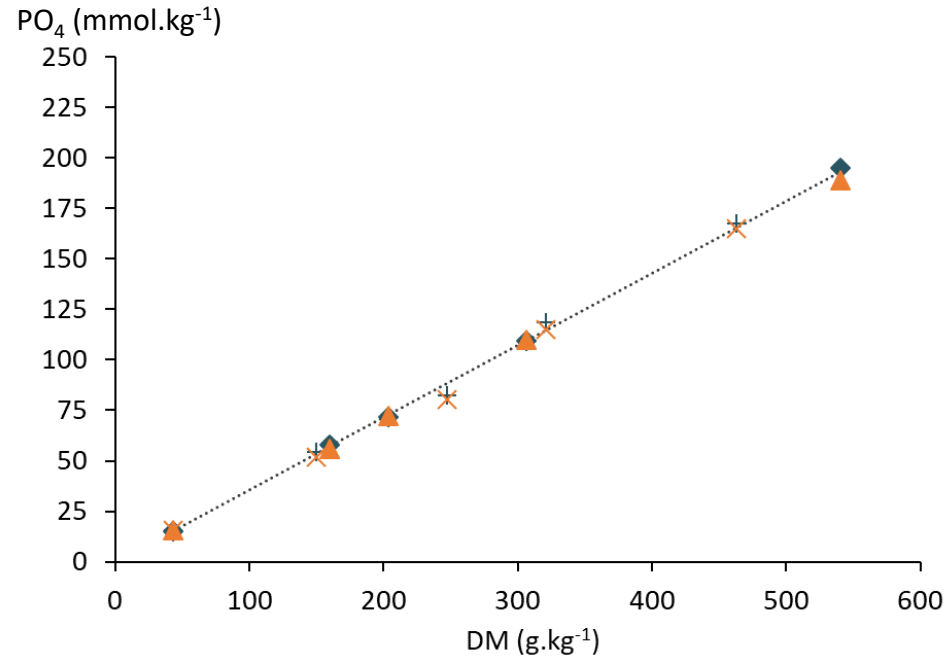
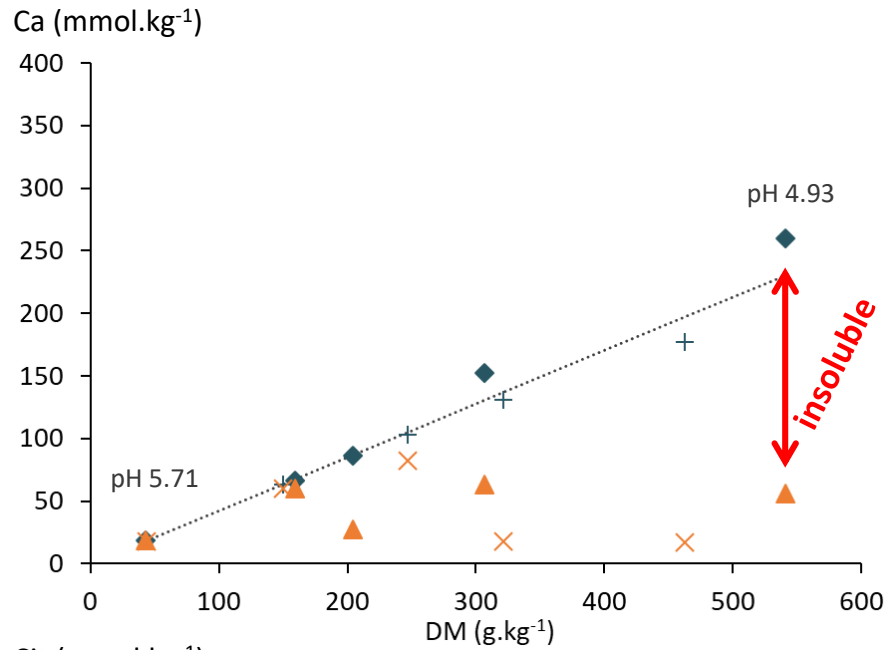
Experiment: Ca & PO<sub>4</sub> precipitated = 62 and 38 mM



: Ca & PO<sub>4</sub> precipitated = 62 and 34 mM

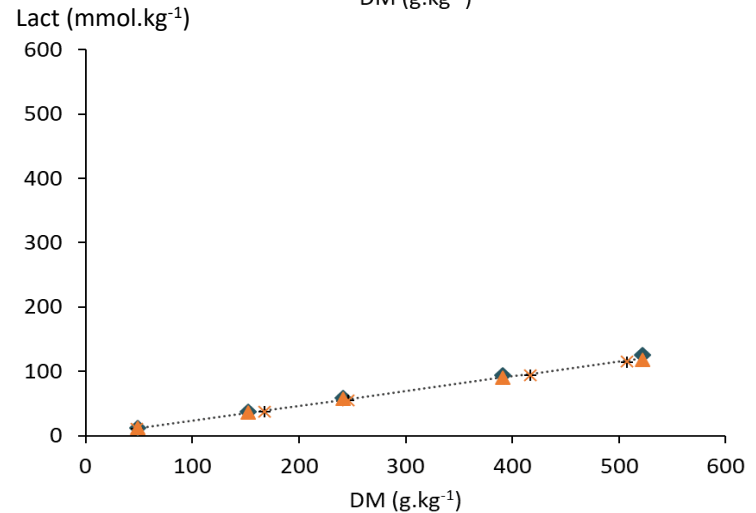
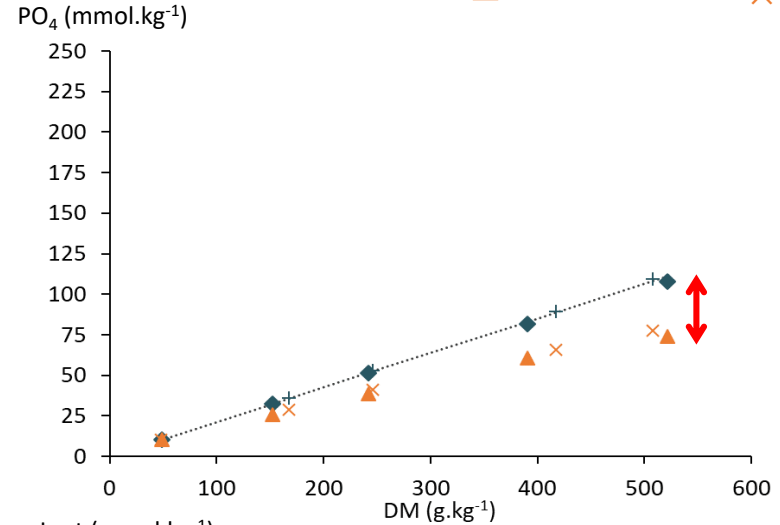
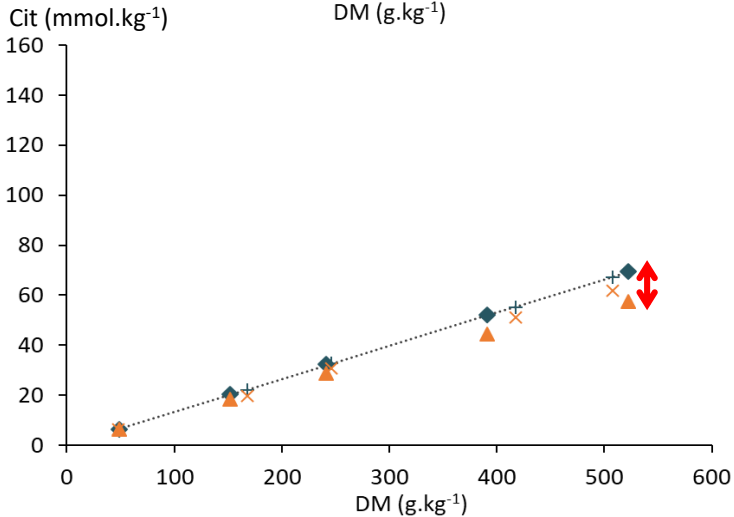
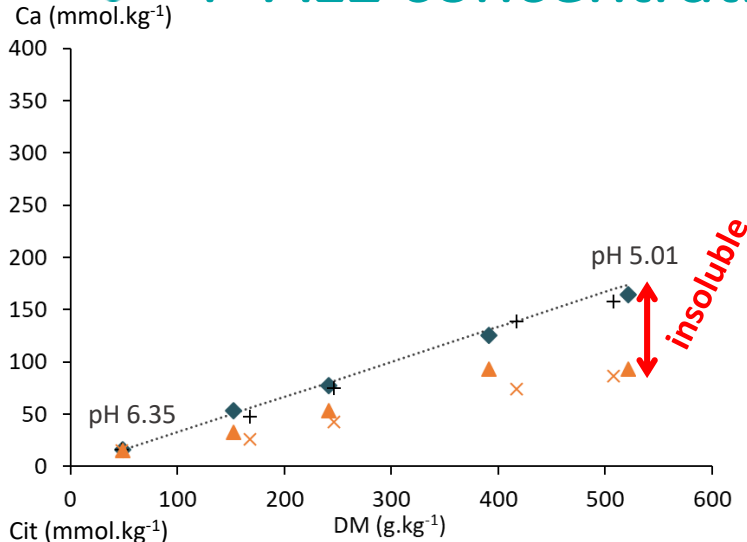
# ➤ P-ACit concentration

ion content set #1    ion content set #2  
 ◆ total            + total  
 ▲ soluble          × soluble



- Higher contents of Ca, PO<sub>4</sub> and Citrate
- Strong chelating capacity of citrate with calcium (CaCit<sup>-</sup> 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



ion content set #1    ion content set #2

◆ total                    + total

▲ soluble                  × soluble

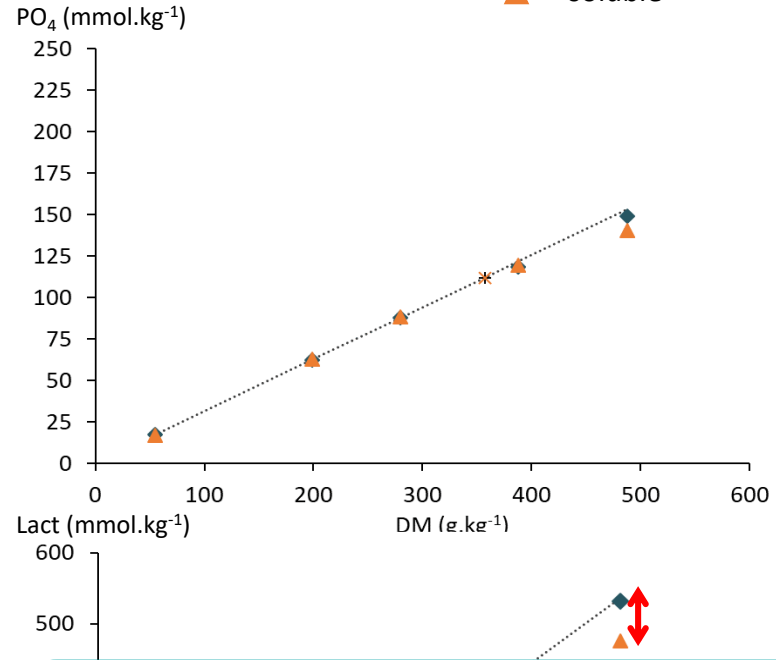
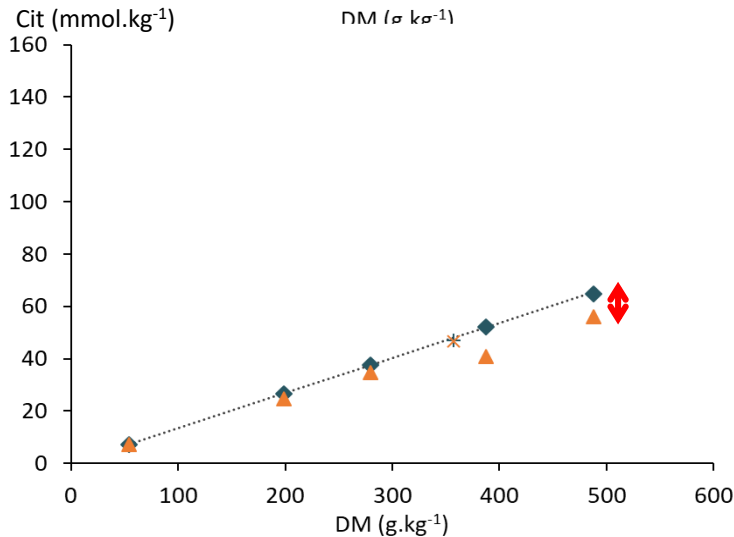
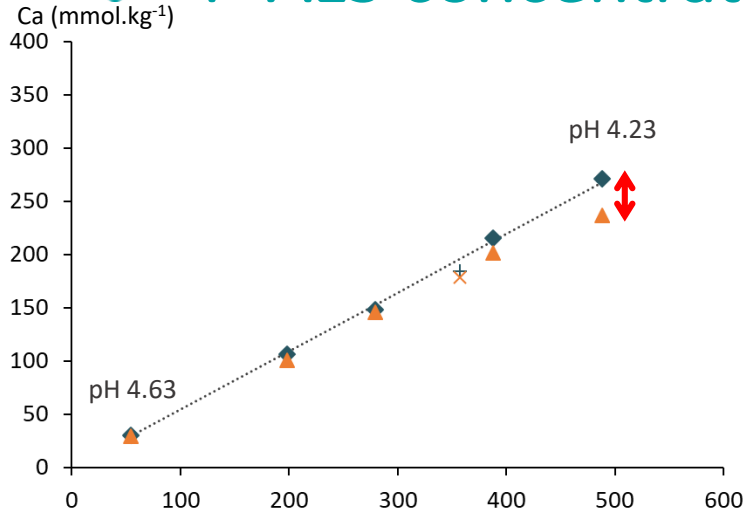
- Situation quite similar to PUF concentration
- Phosphate ion under the form HPO<sub>4</sub><sup>2-</sup>
- Free lactate ion (little affinity to calcium)

Experiment: Ca & PO<sub>4</sub> precipitated = 95 and 52 mM



: Ca & PO<sub>4</sub> precipitated = 93 and 51 mM

# P-AL3 concentration



ion content set #1  
 ◆ total  
 ▲ soluble

ion content set #2  
 + total  
 × soluble

- high lactate content + resulting formation of CaLact<sup>-</sup> 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<sub>2</sub>PO<sub>4</sub><sup>-</sup>) with calcium

## Calcium distribution in initial P-AL3:

Free Ca (50%) CaLact (23%)

CaCit<sup>-</sup> (9.4%)

CaHCit<sup>-</sup> (5.8%) CaCl<sub>2</sub> (4.7%) CaH<sub>2</sub>PO<sub>4</sub> (5.9%)

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



# ➤ 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  $\text{HPO}_4^{2-}$
- **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

*Thank you for  
your attention !*

