facts

Citrates reduce heat-related fouling deposits in high calcium dairy products

Jungbunzlauer
From nature to ingredients®

Abstract

This technical paper benchmarks three important calcium salts used for fortification of dairy and infant formula plus the usage of the pH regulator tripotassium citrate with regard to their effect on unwanted fouling deposits during heat treatment. In a model system, 0.6g of calcium from either calcium carbonate, tricalcium phosphate or tricalcium citrate was added to 1l of whole milk which was heat /UHT treated in lab and pilot scale. Fouling deposits developed in all trials and were measured quantitatively via a sample finger device which was put after the plate heat exchanger. However, calcium carbonate led to massive fouling in the heat exchanger both with and without tripotassium citrate addition and needed to be excluded from quantitative measurement. Jungbunzlauer tricalcium citrate type M2090 (90%<20µm) showed the least fouling deposits, followed by Jungbunzlauer tricalcium citrate type M1098 (98%<10µm) and tricalcium phosphate. Adding 2.2g/l TPC in addition to the aforementioned TCP and TCC salts lead to overall strong decreases in fouling deposits of min. 74% vs. the respective calcium salt without TPC. The best combination was tricalcium citrate M2090 with tripotassium citrate, generating 96% less fouling.

Introduction

Calcium carbonate (CC), tricalcium phosphate (TCP) and tricalcium citrate (TCC) are established calcium salts for calcium fortification of dairy products, particularly infant formula. However, added calcium salts may induce deposits during the heating step (i.e. fouling) which pose challenges to effective processing. These challenges are lower throughput, increase of cleaning time and intervals as well as wear and tear of the equipment. With this project we wanted to benchmark aforementioned calcium salts by quantifying fouling deposits which are formed during UHT processing of milk as in a model system. In a second set of trials, the influence of the addition of tripotassium citrate (TPC) as buffering agent was tested to check if fouling could be further influenced.

Table 1: **Overview of Jungbunzlauer citrate salts and other calcium salts generally used in infant formula and/or used for the trials (all salts are approved minerals for infant formula and baby food according to Codex and EU legislation)**

		Abbr.	Solubility at RT (g/l)	Used in trials
Mineral salts - Jungbunzlauer	Trisodium Citrate	TSC	420	
	Tripotassium Citrate	TPC	1780	X
	Tricalcium Citrate	TCC	1	X
	Trimagnesium Citrate	TMC	200	
	Zinc Citrate	ZC	3	
Calcium salts - benchmark	Calcium carbonate	CC	Negligible	X
	Tricalcium phosphate	TCP	Negligible	X

The model matrix contained milk (3.5% fat) with approx. 1200 mg/l natural calcium content plus 600 mg/l added calcium salt calculated as calcium and 2.2 g/l added TPC as pH regulator.

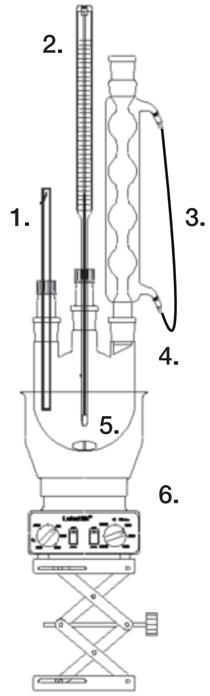
Jungbunzlauer

From nature to ingredients®

Lab trials

In a first step the fouling properties of the different salts were qualitatively assessed in a lab scale pre-trial. A three-neck round-bottom flask, stirred while being heated to 105°C in an oil bath, was filled with the aforementioned model matrices. The pH was measured before and after heating and dropped from approx. 7 to as low as 6.2 (table 2). After 60 minutes the layer on the glass was visually observed (figures 1-2).

Figure 1: Schematic view of lab trial equipment setup



1. pH-Meter
2. Thermometer
3. Cooling
4. Three-neck round-bottom flask
5. Product + magnetic stirrer
6. Oil bath

Figure 2: Calcium induced fouling deposits after lab trial with added TCC (left) and added CC (right)

Jungbunzlauer
From nature to ingredients®

Table 2: **Overview of samples prepared and level of fouling in lab trials. 0 = no fouling, 1 = thin fouling layer, 2 = medium fouling layer, 3 = severe fouling incl. burnt particles.**

Trial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Mineral salt	g/liter milk	g/liter milk	g/liter milk	g/liter milk	g/liter milk	g/liter milk	g/liter milk	g/liter milk
TCC M2090	-	3				3		
TCP	-		1.9				1.9	
CC	-			1.6				1.6
TPC	-				2.2	2.2	2.2	2.2
pH start	6.7	6.7	6.7	6.6	6.8	6.8	6.9	6.8
pH @ 90°C after 60 min	6.2	6.2	6.3	6.2	6.5	6.5	6.5	6.5
Fouling observation	2	2	3	3	1	1	1	3

The addition of calcium had an effect on the layer level in the flask, which was highest for calcium carbonate, followed by TCP without added TPC buffer. The influence on the pH during heating was notable (Δ ~0.8) and less pronounced when TPC was added as a buffer (Δ ~0.5). It is worth mentioning that generally the cleaning and the handling of the samples with added TPC were much easier.

Pilot plant trials

More detailed trials were done using a pilot-scale plate heat exchanger in collaboration with the Landwitschaftliches Zentrum, Milchwirtschaft Wangen, Germany. The pilot unit (Figure 3) was a batch UHT- pasteurizer with inline homo-genization, plate heat exchanger, bypass after heating and before cooling and outlet (Figure 4). The pasteurizer unit included a sample finger device with a surface area of 23.5cm², which was located in the bypass after the heat exchanger plates to collect fouling deposits (figure 2). The salts were added in the same concentration like in the lab trials (600 mg Ca/l, plus 2.2g/l TPC) while being stirred in 100l of control milk (3.5% fat). The following parameters where monitored during processing:

- Temperature and filling speed
- Visual inspection of heat exchanger plates and sample finger before and after heat treatment
- Weight of sample finger before and after heat treatment
- pH

To check the possible influence of particle size, we also included TCC M1098 in addition to TCC M2090. As it can be seen in Table 3, all products had particles sizes in a range of min. 90% < 20µm with TCC M1098 being the finest product.

Table 3: **Particle sizes of insoluble calcium salts tested**

		Particle size
Calcium salts - Jungbunzlauer	TCC M1098	98% < 10µm
	TCC M2090	90% < 20µm
Calcium salts - benchmark	CC	98% < 15µm
	TCP	90% < 20µm

Figure 3: Weighing of the sample finger without fouling deposit

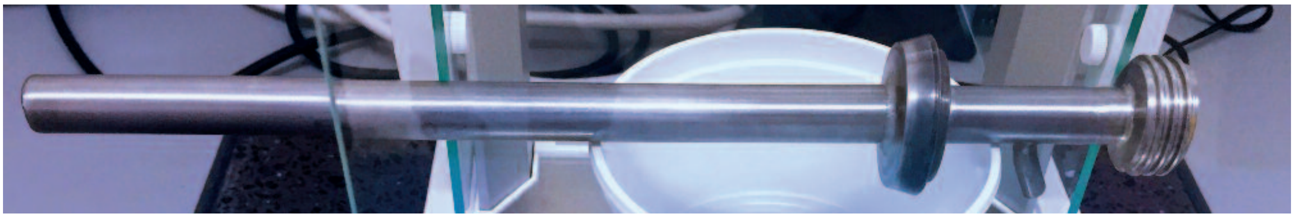
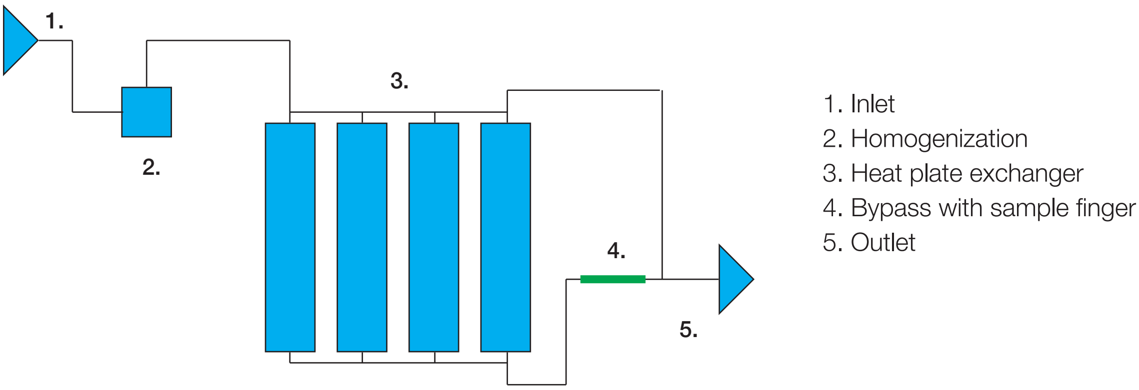


Figure 4 : Pilot plant with modified pasteurizer



Temperature and filling speed

The temperature was set to 140°C for 6 seconds from start to end of filling. Depending on the salts tested, the temperature fluctuated between -10 and +10°C. In the trials, the filling of control milk was in the range of 1.2m/s, whereas it decreased to 0.3m/s for the sample run with TCP and TCC. However, the sample run with CC behaved differently due to pressure getting too high and thus the necessity to reduce filling speed below 0.3m/s and finally to a full stop.

Visual inspection of heat exchanger plates and sample finger before and after heat treatment

The visual inspection indicated fouling deposits on the sample finger with TCP and TCC variants, but not with the CC variants. This was contradictory to what was observed in the lab. Thus, the visual inspection of the plate heat exchanger after each trial needed to also be taken into account (table 4). There was a clear difference of fouling deposits in the CC trials vs. all other trials. Only here, severe fouling occurred in the heat exchanger, so fouling could not be measured on the sample finger. Thus, only the quantitative data of the sample finger from the remaining trials with TCP and TCC vs. control are relevant and were further considered.

Jungbunzlauer
From nature to ingredients®

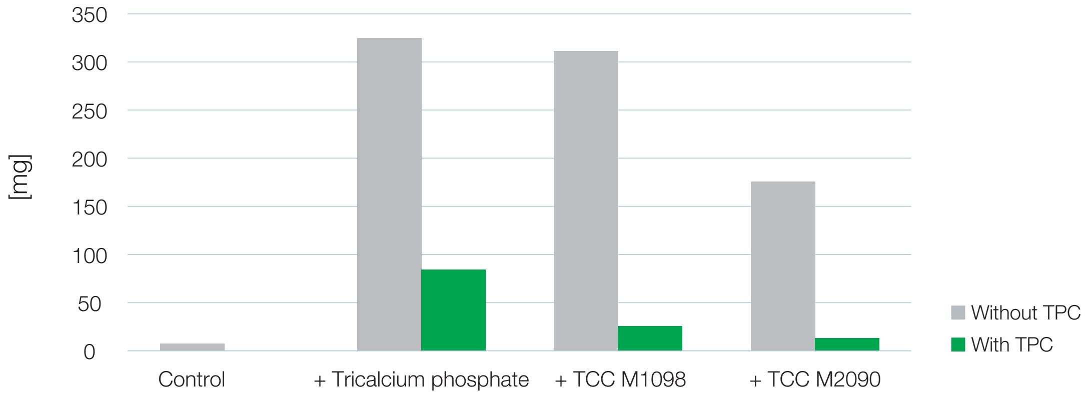
Table 4: **Visual inspection of UHT heat exchanger plates and sample finger after each trial run.**
0 = no fouling, 1 = thin fouling layer, 2 = medium fouling layer, 3 = sever fouling including burnt particles.

Trials without TPC	Fouling heat exchanger	Fouling sample finger
Control	1	0
CC	3	0
TCP	2	2
TCC M1098	2	2
TCC M2090	2	2
Trials with TPC	**Fouling heat exchanger**	**Fouling sample finger**
Control	1	1
CC	3	0
TCP	2	2
TCC M1098	1	1
TCC M2090	1	1

Weight of sample finger before and after filling

Generally, the equipment set-up was suitable for heat treatment of whole milk as the control showed low fouling. In all three trials for which TCP or TCC was added without TPC, an increase in fouling deposits were recorded (figure 5). Results were comparable between TCC M1098 and TCP. However using TCC M2090 reduced fouling deposits compared to finer TCC M1098 by 44%. It can be assumed that the coarser M2090 is less reactive and thus forms fewer fouling deposits due to its lower solubility kinetics related to the lower surface to volume ratio of the dispersed particles. This fits to the experience of Jungbunzlauer's customers who prefer TCC M2090 over M1098 in wet processing of dairy and infant formula products. Interestingly, TCC M2090 shows similar particle size to TCP whilst generating 46% less fouling deposits. This could be explained by the higher solubility of the phosphate at these temperatures and thus the higher reactivity of the calcium salt being in the phosphate vs. the citrate form.
Adding TPC in addition to the aforementioned TCP and TCC salts lead to overall strong decreases in fouling deposits in the range of 74-96% vs. the respective calcium salt without TPC. Clear differences can be seen again between TCP vs. M2090 and this time also vs. TCC M1098 (67% and 92% less deposits, respectively).

Figure 5: Weight difference of sample finger (mg) before and after heat treatment, resembling fouling deposit

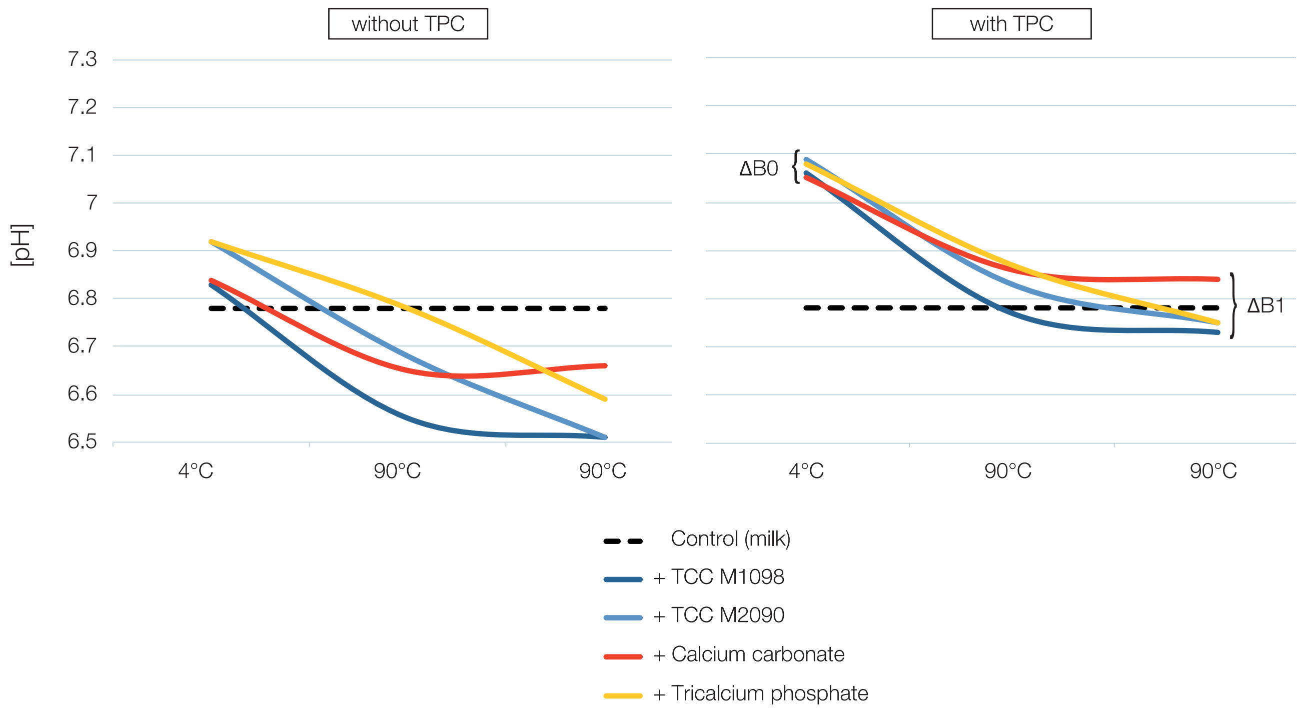


Jungbunzlauer
From nature to ingredients®

pH

The pure milk at 20°C before UHT had a pH of 6.9, the addition of the calcium salts increased the pH up to 7.1 (highest measured value). The pH decreased during the filling (measured after 50l milk filled) from 6.9 down to 6.5 (lowest measured value). The pH by the end of filling (100l at ~142°C and cooled down to 20°C) did not significantly change (data not shown). Figure 6 shows the changes in pH for each trial of calcium fortified milk vs. control with and without TPC addition. Whereas heat treatment does not influence the pH of control milk, pH is strongly affected in the presence of insoluble calcium salt. Interestingly, all added calcium salts lead to a slight alkalization at starting temperature 4°C, followed by a stronger pH drop during heat treatment, which is known to be detrimental to milk stability. This drop is much more pronounced without the addition of TPC, leading to a final pH around 6.6. TPC seems to act as a buffer, reducing fluctuations of start and end pH (ΔB0 vs. ΔB1) and at the same time keeping pH around 6.8 and thus close to the control. This more stable pH could serve as the most important explanation for the strong reduction of fouling deposits in the trials where TPC was used.

Figure 6: pH of control milk compared to calcium fortified milk with and without TPC addition during heat treatment



Outlook

Combinations of TCC and TPC worked very well in these trials related to dairy products. Soy milk is another food which is frequently calcium fortified and can also have fouling issues during processing. Thus, Jungbunzlauer very recently performed new follow-up trials in Wangen, Germany with soy milk which will be published separately.

Jungbunzlauer
From nature to ingredients®

About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality. Our mission "From nature to ingredients®" commits us to the protection of people and their environment.

The Authors

Martin Schottenheimer – Team Leader Food Application Technology, Jungbunzlauer Ladenburg GmbH

Florian Gutschalk – Project Manager Food Application Technology, Jungbunzlauer Ladenburg GmbH

Dr. Gerhard Gerstner – Business Development Director Health & Nutrition, Jungbunzlauer Ladenburg GmbH

HealthyChoices@Jungbunzlauer.com

Discover more on
www.jungbunzlauer.com

Headquarters **Jungbunzlauer Suisse AG** · CH-4002 Basel · Switzerland · Phone +41-61-2955 100 · headquarters@jungbunzlauer.com

www.jungbunzlauer.com

Jungbunzlauer
From nature to ingredients®