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Introduction > The global functional foods market is dominated by dairy products, with sales valued at 9.23 bn USD in 2010 [1]. Despite already being a well-developed market in many countries, manufacturers are continuing to innovate, driven by the consumers demand for products that fit into their diet and nutritional needs. In consequence, the scope for the growth of new, innovative, and healthier products is steadily increasing [2, 3]. This success is based on various pillars. In general, dairy products are perceived to be healthy and fortification makes them even healthier. They are a popular part of the diet and their consumption is a daily routine. This favours their usage as a carrier for functional foods that should be consumed regularly. Milk products are already a good source of calcium and fortification leads to products that can contribute more than 50 % of the daily requirements to the diet.

Functional dairy products have been impacted in the EU by the recent health claims regulation, as the usage of claims on popular functional ingredients like pro- or prebiotics is restricted. However, there is still room in the market for new products [3]. Especially minerals like calcium, magnesium or zinc can offer a wide range of claim options that address the top health topics like bone health, immunity, energy or cognitive functions. These health benefits can be clearly defined and are easy for the consumer to understand. Recent examples like “Yoplait Calin+” or “Danone Densia” underline what is still possible in the market. Containing 50 % RDA of calcium per serving plus vitamin D and referring to bone health, these products set a new benchmark for calcium fortified yoghurts.

However, feasibility of mineral addition has to be considered, as milk products are a complex food matrix and high fortification levels are challenging. With the right selection of the appropriate mineral compound and the proper application success is possible.

Based on our history and expertise on mineral fortification, Jungbunzlauer has recently started a cooperation with the University of Hohenheim in Germany to fully understand the applicability of mineral salts in dairy products [4].

This article discusses important nutritional and technological aspects of mineral fortification of dairy products. It provides the major findings of our internal lab work and our cooperation with the University of Hohenheim with specific focus on calcium, magnesium and zinc fortification in milk, yoghurt as well as drinking yoghurt.

Challenges > Milk is an important source of minerals in our diet and about 40% to 74% of daily calcium is provided by dairy foods [5]. Together with magnesium, potassium and sodium, calcium plays an important role in the structure and stability of casein micelles. In whole milk, about two thirds of its calcium and one third of its magnesium is bound in the micelle and the remaining mineral fractions are dissolved in the aqueous phase [6]. Mineral supplementation of milk is challenging, because the soluble phase is considered to be saturated at its normal pH, making further addition difficult [7].

Therefore, selection of the appropriate mineral source for a specific application is extremely important. Commonly used calcium, magnesium and zinc salts in dairy applications are shown in table 1.

Properties of the respective mineral compounds such as mineral content¸ solubility and taste are essential parameters for product development while bioavailability and economic considerations are also of high importance.

Suitable mineral salts can roughly be subdivided into soluble or insoluble minerals. When using soluble salts, sedimentation and influence on mouth feeling are negligible at first sight, while impact on taste and pH value is increasing with rising fortification levels. However, pH changes and the additional free ions can destabilise the system especially during heat treatment. This may lead to coagulation, syneresis and reactions with further ingredients of the milk product like phosphate and proteins [8]. Addition of chelating agents such as potassium citrate has been shown to enable higher fortification levels by adjusting the pH level, chelating free cations as well as competing with calcium to reduce cross-linking [7].

In contrast to soluble minerals, low or insoluble minerals remain mainly dispersed within the product, thereby having much lower impact here on the dairy matrix. In addition, their influence on taste is less pronounced, as bitter and astringent off-tastes are related to free ions of dissociated minerals. While being mainly suspended, insoluble minerals can affect mouth feeling in terms of grittiness and chalkiness, and can lead to sedimentation in low viscous products. Micronised mineral salts are a good option to address these undesired effects. Speed of sed-

Table 1. Overview of calcium, magnesium and zinc salts approved for fortification in Europe acc. to Regulation (EC) No. 1825/2006

	Compound	Mineral Content	Solubility	Taste
Ca	Calcium Carbonate	40 %	Insoluble	Soapy, lemony
	Calcium Chloride · 2 H_2O	27 %	745 g/l	Salty, bitter
	Calcium Lactate · 5 H_2O	14 %	90 g/l	Bitter at high concentrations
	Calcium Lactate Gluconate (as Calcium Lactate & Calcium Gluconate)	13 %	400 g/l	Slightly bitter at high conc.
	Tricalcium Citrate · 4 H_2O	21 %	1 g/l	Tart, clean
	Tricalcium Phosphate	40 %	Insoluble	Sandy, bland
Mg	Magnesium Carbonate basic · 5 H_2O	24 %	4 g/l	Earthy
	Magnesium Lactate · 2 H_2O	10 %	70 g/l	Neutral
	Magnesium Sulfate · 7 H_2O	10 %	710 g/l	Saline, bitter
	Trimagnesium Citrate · 9 H2O	12 %	16 g/l	Neutral
	Trimagnesium Citrate anhydrous	16 %	200 g/l	Neutral
	Trimagnesium Phosphate · 5 H2O	21 %	Insoluble	Neutral
Zn	**Zinc Citrate · 3 H2O**	31 %	3 g/l	Slightly bitter
	Zinc Gluconate · x H_2O	13 %	100 g/l	Bitter, astringent
	Zinc Oxide	80 %	Insoluble	Bitter
	Zinc Sulfate · 7 H2O	23 %	960 g/l	Astringent, bitter, metallic

Source: Internal evaluation and [7]; Jungbunzlauer products are marked in bold

imentation is reduced by decreasing particle size and ultrafine particles are no longer perceived. Particles significantly smaller than 20 µm allow fortification levels far above the ones achievable with dissolved minerals.

Bioavailability > Any nutrient's effectiveness depends on its bioavailability, meaning how well the human body absorbs and utilises it. Mineral bioavailability from food sources can vary from e.g. 10–30% for calcium, 40–60 % for magnesium or 5–50 % for Zinc [7]. Several scientific studies indicate that organic mineral salts like citrates, lactates or gluconates outperform inorganic mineral sources such as oxides, carbonates and phosphate with regard to their relative bioavailability [9, 10].

Fortification of milk > When fortifying milk, solubility, dissolution characteristics, sedimentation behaviours and stability of the final formulation are major challenges. Organic calcium salts like calcium gluconate, calcium lactate, or calcium lactate gluconate and inorganic calcium chloride are highly soluble, but their use is limited due to off tastes at higher concentrations. Having the lowest taste impact within the range of soluble calcium salts, calcium lactate gluconate can be added to achieve 200 mg of total calcium to 100 ml milk without a significant influence on its taste. Due to their influence on pH value and the contribution of free calcium ions, products tend to be unstable during heat treatment. However, with the addition of tripotassium citrate the system can be stabilised, but the effect is limited to lower fortification levels. As a new route, addition of sterilised or ultrafiltrated mineral solutions after the heat treatment step is a recommended alternative and results in stable fortified UHT milk (Figure 1).

Inorganic calcium carbonate and calcium phosphate are insoluble. The organic tricalcium citrate in the commonly used tetrahydrate form shows a slight solubility of 1 g/l while having low effect on product pH value and thus minor effect on product stability, even when applied at higher concentrations. Tricalcium citrate shows an "inverse solubility", i. e. it is more soluble at lower and less soluble at higher temperatures. The latter is beneficial during heat treatment, as the risk of coagulation can be further reduced (Figure 1).

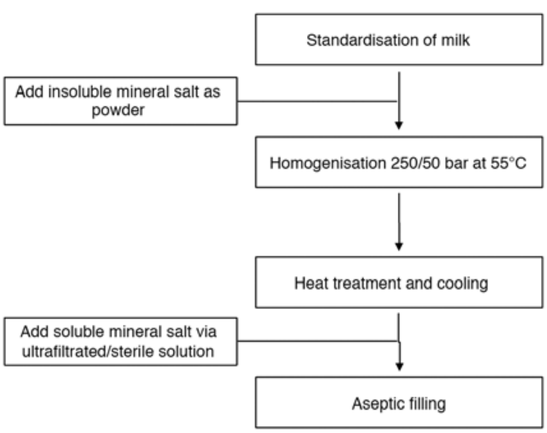

Fig. 1: Process flow chart for fortified UHT milk

However minerals with low solubility tend to sediment during storage. Usage of micronised forms improves dispersion during addition, helps to keep particles in suspension longer and results in better mouth feel. Jungbunzlauer's M1098 (98 % < 10 µm), the finest available micronised grade of tricalcium citrate, allows to increase the calcium content of plain milk up to 200 mg/100 ml (25 % EU RDA) without negative taste effects.

Sedimentation behaviour can be further improved, by increasing the viscosity of the milk. In our trials, the addition of kappa carrageenan has shown the most promising results. At above mentioned fortification levels sedimentation can still appear, but ultrafine tricalcium citrate typically shows good re-dispersability compared to other calcium forms.

In contrast to calcium, magnesium fortified milk products are less common and available literature is limited. Being also a bivalent cation, the addition of magnesium salts has shown similar behaviour as in case of calcium according to our experience. Various liquid milk products contain readily soluble magnesium salts like organic trimagnesium citrate anhydrous or magnesium lactate and inorganic magnesium sulfate. They also destabilise the milk matrix during heat treatment. In this respect, tripotassium citrate improves heat stability and enables a fortification to 210 mg magnesium per 250 ml serving (55 % EU RDA). Addition of trimagnesium citrate anhydrous after heat treatment allows similar or even higher magnesium contents, without need for stabilising via tripotassium citrate. Surprisingly, the fortification showed positive effects on the taste profile of milk. In contrast, addition of magnesium sulfate had a negative taste impact.

Insoluble magnesium salts like inorganic magnesium carbonate and magnesium phosphate or low soluble organic trimagnesium citrate nonahydrate show sedimentation during storage. As with tricalcium citrate, addition of kappa carrageenan can reduce sedimentation. However, as fortification is feasible in homogeneous phase at reasonable levels with trimagnesium citrate anhydrous, whilst even improving the taste profile, insoluble salts are considered as secondary choice.

Due to the low RDA and thus the low usage levels of zinc salts, solubility is not a major issue in fortified milk products. The range of zinc salts for milk fortification comprise high soluble inorganic zinc sulfate or organic zinc gluconate and zinc lactate, as well as low soluble zinc citrate (2.6 g/l) and insoluble zinc oxide. While the soluble zinc salts are fully dissolved, the presence of organic anions like gluconate, lactate or citrate help to reduce negative taste effects like bitterness and astringency associated with free zinc ions.

Fortification of yoghurt > When fortifying high viscous dairy products such as yoghurts, Greek yoghurt or curd cheese (petit Swiss) organoleptic properties like taste or mouth feel are major issues. Soluble minerals are of minor importance as dissolution is not required and negative effects on taste dominate at higher concentrations. Minerals are generally applied via the fruit preparation (Figure 2). Their low pH value and high citric acid/fruit acid concentration increase mineral solubility. On one hand this can help to facilitate a proper distribution. On the other hand when inorganic minerals like carbonates or phosphates are used, a neutralisation reaction between free calcium ions and abundant citric acid may take place over time. This may result in an uncontrolled de-novo growth of especially calcium citrate crystals, which leads to grittiness, destabilises the fruit preparation and impacts the mouth feel and shelf life of the fortified yoghurt. In our trials, yoghurts fortified with mineral citrates do not show such a phenomenon.

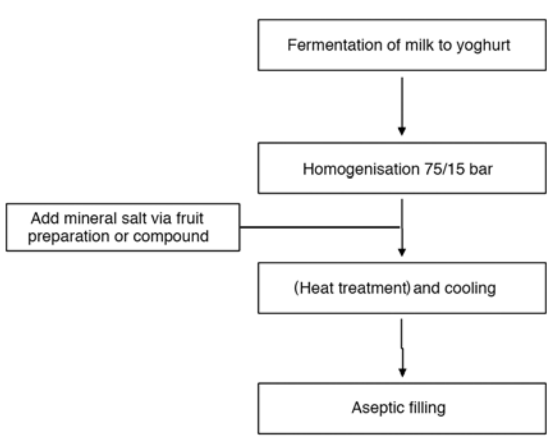

Fig. 2: Process flow chart for fortified yoghurt

With increasing fortification, micronisation of minerals is indispensable. Ultrafine particles ease dispersion and reduce sedimentation within the fruit preparation and improve texture and mouth feel of the final product. Jungbunzlauer's tricalcium citrate can even be suspended in yoghurts at concentrations of more than 500 mg calcium per 125 mg serving (62.5 % EU RDA). In case of magnesium and zinc similar or even higher RDA can be achieved with trimagnesium citrate and zinc citrate.

In plain yoghurts, a liquid mineral suspension can be applied and the addition of starch has shown to stabilize these suspensions by reducing sedimentation.

Fortification of drinking yoghurt > Drinking yoghurt holds an intermediate position between milk and yoghurt products. Produced from yoghurt, it has a pH similar to yoghurt (~pH4) while the viscosity tends to be much lower. Like yoghurts, these products are best fortified via fruit preparations. As the addition of low or insoluble minerals is preferred, sedimentation may become a challenge. Besides the usage of micronised minerals also viscosity adjustment is of high importance. Options comprise:

- Usage of exopolysaccharide cultures for the fermentation
- Higher usage levels of pectin in fruit preparations
- Reduction of added water
- Reduction of the homogenisation pressure (e.g. 75/15 bar)

A viscosity above 225 mPa*s enables fortification levels similar to the ones achievable in yoghurt.

Table 2: Recommended mineral salts and maximum fortification levels in milk, yoghurt and drinking yoghurt

Application	Recommended mineral salt	Max. fortification level (EU RDA)	Recommendations
Milk	Calcium Lactate Gluconate	500 mg/250 ml Ca (63 %)	Addition of mineral salt after heat treatment.
	Tricalcium Citrate M1098	500 mg/250 ml Ca (63 %)	Addition of kappa carrageenan (0.025 %).
	Trimagnesium Citrate Anhydrous	200 mg/250 ml Mg (53 %)	Addition of mineral salt after heat treatment or addition together with Tripotassium Citrate (0.3 %) before heat treatment.
	Zinc Citrate	7.5 mg/250 ml Zn (75 %)	
Yoghurt	Tricalcium Citrate M1098	500 mg/125g Ca (63 %)	Plain yoghurt: Addition of minerals together with starch (Ultra Sperse 5; 0.08 %). Fruit yoghurt: Addition of mineral to fruit preparation.
	Trimagnesium Citrate Nonahydrate	200 mg/125g Mg (53 %)	
	Zinc Citrate	7.5 mg/125g Zn (75 %)	
Drinking Yoghurt	Tricalcium Citrate M1098	500 mg/100 ml Ca (63 %)	Addition of pectin (H&F CM 201; 0.35 %)
	Trimagnesium Citrate Nonahydrate	120 mg/100 ml Mg (30 %)	
	Zinc Citrate	7.5 mg/100 ml Zn (75 %)	

Summary of results > Table 2 provides the key findings of our trials in various dairy matrixes. This toolbox serves as a guidance to develop new product concepts with magnesium, calcium, zinc or blends thereof with fortification levels up to 75 % EU RDA. Our trials show that high fortification of milk, yoghurt as well as drinking yoghurt is feasible, without compromising taste or product stability.

Outlook > The challenge for dairy product manufacturers is to provide products with highest mineral content and appealing sensory properties. Since micronised tricalcium citrate has been available, it has replaced inorganic as well as organic salts such as calcium lactate in dairy applications and enabled manufactures to fortify products to more than 50 % RDA of calcium per serving. The combination of outstanding technological properties and high nutritional value (bioavailability) makes micronised tricalcium citrate the number one option for calcium fortified milk products [11]. In contrast to calcium, fortification with magnesium and zinc is not as established in the market. Especially in Europe, where health claims on products are regulated by the new EFSA health claim regulation, magnesium and zinc offer various options for new product concepts. With the raising awareness for these two minerals and their various beneficial effects on human health they should gain importance in dairy products soon as such or together with calcium and other nutritional ingredients. As technological hurdles will increase with higher fortification levels, trimagnesium citrate and zinc citrate will be able to prove their superior performance in dairy applications.

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