

How to Fortify Beverages With Calcium

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Along with current developments of the overall functional foods market, the use of minerals and especially calcium salts is expected to exhibit strong growth rates. In contrary to other functional ingredients, calcium is widely known as being beneficial for human health and there is no need to explain its nutritional advantages to the customer. According to Leatherhead International, future trends include growing consumer concern regarding osteoporosis and bone health, leading to increased sales of calcium salts. The continuous market growth drives mineral salt suppliers to offer not only one product but rather a range of different calcium salts and granulations to be able to tune them to industrial customers' applications. This article discusses important nutritional, technological as well as economical aspects of calcium in beverages with a focus on our company's products Tricalcium Citrate, Calcium Gluconate and the new product development Calcium Lactate Gluconate.

Optimizing calcium intake

Calcium is a key mineral in the human body, necessary for normal growth and development of the skeleton as well as for teeth, nerve, muscle and enzyme functions. As the body's calcium absorption capabilities reduce with age, it is vital for the ageing to have a sufficient calcium intake. Calcium requirements vary throughout an individual's life and for different population groups. However, it is generally evident that a significant proportion of the population in Western countries fails to achieve the recommended calcium intakes. Poor dietary habits are seen to be responsible for this situation, especially if consumption of fast food is dominating the daily menu.

Various studies showed that a significant proportion of the population groups fails to achieve the calcium intakes in western countries¹. This



observation is seen as being one of the main factors causing osteoporosis². As a consequence, national authorities all over the world have recently reconsidered recommendations in order to take remedial measures against calcium deficiency and accordingly, to reduce the risk of osteoporosis. In this respect, the US National Institute of Health (NIH) has increased the amounts of optimal daily calcium intake and defined specific values for each population group³. For example, calcium intake should be 1000 mg/day for adults (25-65 years of age) and as much as 1500 mg/day for seniors (older than 65 years) or lactating women. Harmonization of Recommended Daily Allowances (RDA) is under discussion also on EU level right now and in this context, the Scientific Committee on Food just recently recommended a higher RDA of 1000 mg vs. the existing level of 800 mg calcium per day⁴.

There are several options to avoid calcium deficiency by increasing the daily calcium intake: A balanced diet with calcium-rich foods like milk, dairy products and certain vegetables (broccoli, Chinese cabbage, legumes) would be the best solution. However, this would require a profound change in dietary habits of western society. A further possibility consists in taking calcium supplement products. A more elegant option is consuming "regular" food fortified with calcium as an added value product.

Common calcium sources for beverage fortification

Table 1 shows a typical range of calcium fortified beverages which have been seen in European and US supermarkets recently. Practically every type of beverage such as mineral water, soy milk, energy drink, nectar or juice does have a fortified product line already. Looking at the ingredients list, it is evident that there is not "the" calcium source but rather a range of different possibilities used commercially:

- inorganic salts like calcium carbonate and calcium phosphate
- organic salts like tricalcium citrate, calcium lactate, calcium lactate gluconate and calcium gluconate.

The selection of the appropriate salt for a specific application is usually based on the consideration of a number of properties associated with the respective product such as solubility, calcium content, taste and bioavailability. Economic considerations are another important factor.

Solubility vs. calcium content

When fortifying beverages, solubility, dissolution characteristics and stability of ingredients in solution are a major issue. There are calcium salts with good solubility like calcium gluconate, calcium lactate, and calcium

Table 1. Calcium-fortified clear, cloudy as well as instant beverages found in European and US supermarkets

| Products | Calcium source added | Serving size (mL) | Calcium content (mg/L) | Nutritional claim used on the product label |
|-----------------------------|---|-------------------|------------------------|---|
| 1. Clear beverages | | | | |
| Still mineral water | Calcium carbonate / chloride / sulphate | 500 | 300 | Source of calcium |
| Near water drink | Tricalcium citrate | 500 | 240 | With calcium |
| Apple juice I | Calcium lactate | 125 | 800 | Calcium enriched |
| Apple juice II | Calcium lactate gluconate | 250 | 1200 | With calcium |
| Tangerine orange drink | Tricalcium citrate | 330 | 368 | Plus minerals |
| 2. Cloudy beverages | | | | |
| Apricot nectar | Calcium lactate | 162 | 417 | With calcium |
| Tropical nectar | Tricalcium citrate | 200 | 500 | - |
| Soy milk I | Calcium carbonate | 250 | 1200 | Added calcium |
| Soy milk II | Calcium citrate, calcium carbonate | 500 | 1200 | With calcium |
| Fruit Juice | Calcium lactate gluconate | 240 | 417 | Fortified with calcium |
| Cranberry juice | Calcium lactate gluconate | 240 | 417 | Fortified with calcium |
| Grapefruit juice | Tricalcium citrate | 240 | 1458 | Plus calcium |
| Orange/tangerine juice | Tricalcium phosphate, calcium lactate | 240 | 1458 | As much calcium as milk |
| Orange juice I | FruitCal® | 240 | 1458 | As much calcium as milk |
| Orange juice II | Tricalcium citrate | 414 | 276 | With added calcium |
| Orange juice III | Calcium lactate gluconate, tricalcium citrate | 200 | 1600 | Calcium+ |
| 3. Instant beverages | | | | |
| Instant tea drink | Calcium lactate gluconate | 100 | 1200 | With calcium |
| Beverage powder | Calcium gluconate | 113 | ca. 3550 | Fast absorbing calcium |

lactate gluconate but their drawback is a comparably low calcium content (Table 2). Calcium salts with a high calcium content like calcium carbonate and calcium phosphate, on the other hand, are poorly soluble and for that reason not commonly used in beverages.

Tricalcium citrate offers a good combination: The commonly used tetrahydrate form shows a high calcium level (21 %) and moderate solubility (0.9 g/L). Solubility is strongly influenced by the pH of the system since the solubility of calcium salts typically increases with decreasing pH. Tricalcium citrate shows improved solubility at pH-values below 4.5 as found in most beverages. If calcium content is referred to per beverage serving of 330 or 500 mL, 15 % of RDA (120 mg calcium) can easily be reached with tricalcium citrate also for acidic clear beverages. Contrary to other salts, tricalcium citrate is better soluble at low temperatures which can be an advantage for processing because it can be dissolved at low temperatures and shows low reactivity at high temperatures. To further increase the solubility and ease of dispersion, we have developed a particularly fine (micronized) tricalcium citrate grade. With this special granulation of min. 90 % < 20 microns, it can be suspended in cloudy beverages and

high concentrations of calcium (e.g. 1.5 g Ca/L) can be reached. Accordingly, tricalcium citrate still is seen to be the main choice for fortified orange or grape juice.

Calcium lactate is provided as a pentahydrate, containing 13 % of calcium. It shows good solubility properties and is therefore mainly used in clear beverages to achieve the necessary levels for nutritional claims on calcium. It is known that using calcium lactate in high concentrations may lead to adverse effects in certain applications^{1,5}. Due to the fact that with higher soluble salts, more free calcium ions are in solution and available for reaction than with lower soluble ones, complications in the form of calcium sediments can develop with time. This is the case, when components (e.g. free protein, tartrate or phos-

phate) that give insoluble salts with calcium are present in the product. Thus, although it is possible to add for example more calcium lactate than tricalcium citrate to beverages, higher amounts of calcium in the product might be difficult to achieve without control of pH and addition of chelating agents such as potassium citrate^{1,5}. In some applications, combinations of calcium lactate with other calcium salts can also have a stabilizing effect.

Although calcium gluconate displays a good solubility, it is not used frequently in ready-to-drink beverages, especially due to its low calcium content (9 %). However, its neutral taste properties, good dissolution speed at higher temperatures and low water content makes especially the anhydrous form a valid calcium source for instant prepar-

Table 2. Important characteristics of common calcium sources used in the food industry

| Product | Ca Solubility at 25°C (g/L) | Taste | Calcium Content |
|---|-----------------------------|---------------|-----------------|
| Calcium carbonate | Insoluble | Soapy, lemony | 40 % |
| Calcium phosphate | Insoluble | Sandy, bland | 17 - 38 % |
| Tricalcium citrate (4 H ₂ O) | 0.2 | Tart, clean | 21 % |
| Calcium lactate (5 H ₂ O) | 9.3 | Bland | 13 % |
| Calcium lactate gluconate | 45 - 50 | Neutral | 10 - 13 % |
| Calcium gluconate | 3.5 | Mild, neutral | 9 % |



ations such as fortified beverage powders, enabling high calcium amounts per serving size.

Compared to the above, calcium lactate gluconate is the most soluble salt showing very interesting properties: its solubility is not between the single components calcium lactate and calcium gluconate as one would expect, but it is synergistically enhanced to approx. 400 g/L water. This sums up to a calcium content of 45 to 50 g/L, depending on the ratio of the mixture. With this high calcium value in mind, it is not surprising that this salt is used when a high dissolution speed is required. It is also especially recommended for fortification of clear beverages. The reason for this phenomenon of extremely high solubility is interpreted as the ability of mixtures of lactate and gluconate ions to form metastable complexes with calcium ions in solution, which gives way for additional benefits in beverages: Due to better stability of beverages fortified via calcium lactate gluconate clear beverages can be fortified without the addition of chelating agents⁶. And higher calcium concentrations can be reached, even in critical applications such as grape and cranberry juice, tea beverages and also concentrated pre-blends. Containing approx. 13 %

calcium and 4 % water, our own Calcium Lactate Gluconate can offer an improved formulation compared to other calcium lactate gluconates on the market.

FruitCal[®] is a patented mixture of citric acid, malic acid and calcium hydroxide invented by Procter & Gamble. This highly soluble blend, also called calcium citrate malate is currently used in beverages under license e.g. for Tropicana's (PepsiCo) Pure Premium calcium fortified juices to reach RDA values of calcium comparable to milk.

Taste and mouthfeel

Generally, high levels of calcium, particularly insoluble forms like carbonates and phosphates, tend to produce a chalky mouthfeel and may promote astringency or bitter taste in the finished product. Calcium lactate may impart some bitter or milk-like notes at high concentrations. Calcium carbonate may come across as soapy or lemony. Calcium phosphate has a bland flavor, but imparts a gritty mouthfeel. Negative effects of calcium on taste can be masked with chelating agents (e.g. tripotassium citrate), and the use of stabilizers (e.g. carrageenan) as well as with the addition of flavorings. Tricalcium citrate, cal-

cium lactate gluconate and calcium gluconate are considered to be the most neutral calcium salts, as masking agents are not really necessary.

Since the particle size and solubility are linked with mouthfeel properties, we have developed micronized grades for tricalcium citrate combining excellent dispersion characteristics with a neutral taste profile in final applications.

Bioavailability

Any nutrient's effectiveness depends on its bioavailability, which means how well the human body absorbs and utilizes it. On average, only about 10 to 30 % of calcium is absorbed from a mixed diet by healthy adults⁷. Several different factors influence this level, among which the type of salt which provides the calcium.

Organic vs. inorganic salts

Various scientific studies have shown that organic calcium salts outperform inorganic calcium sources such as calcium carbonate and calcium phosphate with regard to their relative bioavailability. Accordingly, the US National Institute of Health recommended calcium citrate for supplementation, especially for older individuals where absorbability can be a limiting factor due to reduced gastric acid production³. Recently, researchers at the University of Texas conducted a meta-analysis of calcium bioavailability, which evaluated studies on the bioavailability of two of the most common forms of calcium supplements, tricalcium citrate and calcium carbonate⁸. Over 90% of the studies reviewed showed greater absorption of calcium from tricalcium citrate than calcium carbonate by an average of 22 to 27 %.

Similarly, calcium phosphate has also been described in scientific studies to display lower bioavailability than tricalcium citrate⁹. Absorption of calcium from soy milk fortified with tricalcium phosphate reached only 75 % of the efficiency of calcium from cow milk¹⁰. Furthermore, it is not considered to be an appropriate ingredient for calcium fortification due to the undesired characteristics of the phosphate anion. Intake of phosphate is reported to exceed adult RDAs in practically 100 % of the

population¹¹. Therefore, further addition of phosphate to food should be avoided in order to gain a higher calcium-to-phosphorus ratio, which is considered to be favorable for sufficient calcium absorption.

Influence of solubility on bioavailability.

Reviewing the various bioavailability studies which had been done on the common organic salts listed in Table 1, it is concluded that they show similar calcium absorption¹. This holds true even though there are significant solubility differences of organic calcium salts in plain water. Researchers agree that these differences have no significant effect on absorbability in acidic environment such as in gastric acid in the human stomach as well as at neutral conditions in the intestine^{1,9,12}. Although for example tricalcium citrate displays only moderate solubility in water, it had been assessed as having the same solubility in artificial intestinal juice as the calcium lactate¹³. In a recent review of calcium lactate gluconate absorption^{XX}, it was concluded that further to its excellent solubility, it showed a high bioavailability in human studies (30 %) and the most pronounced positive effect on bone mineral density compared to other calcium salts.

Economic considerations vs. calcium content

Although inorganic calcium salts are more economic than organic ones due to their low price and high calcium content, they are not frequently used in beverages anymore. Comparing the mainly used organic sources on the other hand, they are all in the same price range, except for the premium mineral source calcium lactate gluconate. For this reason, their wide range of calcium contents (9 to 21 %) has a considerable impact on the raw material cost when the price of calcium added is calculated for the product to be fortified. Among the organic salts with high bioavailability and more neutral taste profiles, tricalcium citrate (21 % calcium) clearly stands out as the most economic option for calcium addition and is the main choice for cloudy beverages. Calcium lactate has about the same price but a lower

calcium content (13 %). Due to its good solubility, it is a good alternative for clear beverages, if the desired amount of calcium does not affect stability and taste of the beverage. For those critical applications, calcium lactate gluconate (available with up to 13 % calcium) is worth the premium price to achieve high fortification levels, e.g. in clear soft drinks or concentrated pre-blends. Another possibility, having a calcium price between the latter salts, is using highly soluble and neutral tasting calcium gluconate (9 % calcium), e.g. for instant beverage powders.

Conclusion

Consumers increasingly prefer food with added nutritional value rather than taking nutritional supplements to fill up their calcium needs. Beverages with added calcium are seen to be one of the best means to help fighting calcium deficiency and represent a valid nutritional source for people who do not consume dairy or other products high in calcium on a regular basis. However, the challenge for food & beverage manufactures is to provide a product having high calcium content with good taste and appealing properties. Accordingly, Jungbunzlauer as one of the leading producers of citrates and gluconates is further increasing its efforts to provide a wide range of highly bioavailable organic calcium sources for nutritional purposes.

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