Calcium addition to and removal from milk and milk products

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Outline

- Significance of calcium in milk
- Types of calcium in milk
- Calcium addition
  - Calcium fortification
  - Heat-induced gelation & coagulation of milk
  - Whey protein aggregation and gelation
  - Removal of fat from whey
  - Fouling and sediment formation in high-heated milk
- Calcium removal
  - Prevents rennet-induced coagulation
  - Delays age gelation of UHT milk
  - Improves milk protein concentrate stability
  - Improves skim milk powder stability
  - Reduces foaming
  - Allows formation of iron-milk protein complexes

Significance of calcium

- Milk is supersaturated in calcium
- Due to presence in the casein micelle as colloidal calcium phosphate (CCP),
- Excellent carrier of calcium for the newborn.
- Major nutritional benefit of milk and milk products.
- Important in many functional properties of milk and milk products
- But it's a 3 bears situation – sometimes too much, sometimes too little, sometimes just right

Types of calcium

- Total calcium in milk is about 120 mg/100 mL (0.12% or 30 mM)
- 2/3 (80 mg/mL; 20 mM) is bound into the casein micelle
  - Insoluble and non-ionic
  - Mostly colloidal calcium phosphate- the glue that holds the casein micelle together
- 1/3 (40 mg/mL; 10 mM) is in the serum
  - Soluble
    - 32 mg/mL (18 mM) is non-ionic
    - 8 mg/mL (2 mM) is ionic

Calcium addition

Calcium fortification of milk

- Despite the high calcium level in milk, there is interest in adding calcium to milk
- This is tricky because:
  - most soluble calcium salts, like calcium chloride, make milk unstable to heat
  - insoluble salts, like calcium carbonate, tend to sediment out of the milk
- Commercially, insoluble salts are usually added, as very fine powders
- Also, milk minerals and a marine mineral mix are used
- One unique calcium salt is *Gadocal K*® (calcium potassium citrate) which is soluble but stable to heat

Heat- & calcium-induced gelation and coagulation of milk

- Adding a soluble calcium salt (e.g. calcium chloride) and heating milk to ~70°C causes either:
  - a gel (like yogurt) at low concentrations (< 0.3%) of calcium chloride (~0.8 % or 20 mM Ca)
    - forms an attractive desert when flavoured and sweetened
  - a coagulum (like cottage cheese or paneer) at higher concentrations (> 0.3%), with whey separation
    - a milk tofu? (tofu is made by heating soymilk with calcium or magnesium salts)
    - Can be used like paneer in Indian-style dishes
- Neither taken up commercially - yet

Whey protein gelation

Hot gelation

- Over a certain protein concentration (~7%), whey protein concentrate (WPC) or whey protein isolate (WPI) denatures and forms a gel when heated to >70°C
- Calcium ions up to ~ 20 mM (0.3% calcium chloride) strengthen this gel by interacting with/cross linking the protein

Cold gelation

- Adding calcium to whey proteins preheated to 70-90°C forms a cold-set gel

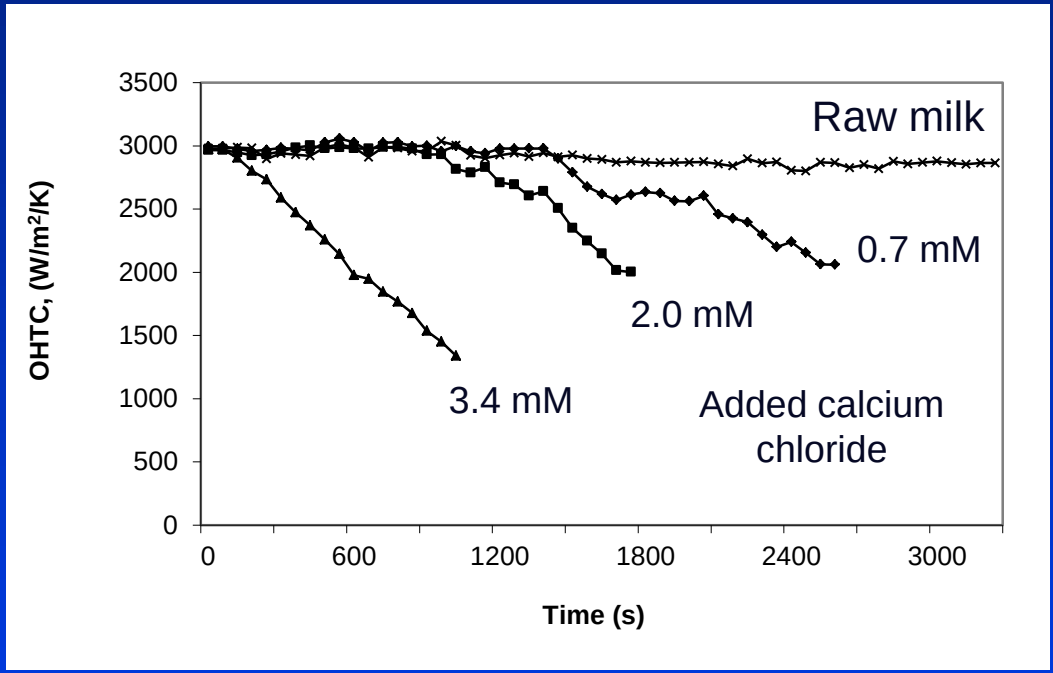
Removal of fat from whey – the thermocalcic method

- Whey contains ~0.5% fat
  - The fat is in small fat globules and membrane material (skim membrane and milk fat globule membrane), which contains polar lipids, e.g., phospholipids
  - The fat causes whey to be cloudy and interferes with ultrafiltration of whey and properties of the whey protein concentrate, e.g., foaming
- The fat can be removed adding calcium chloride (0.3 – 1.2%) and heating (55°C) at pH ~7.5
- Precipitates out > 90% of polar lipids

Fouling and sediment formation in high-heated milk

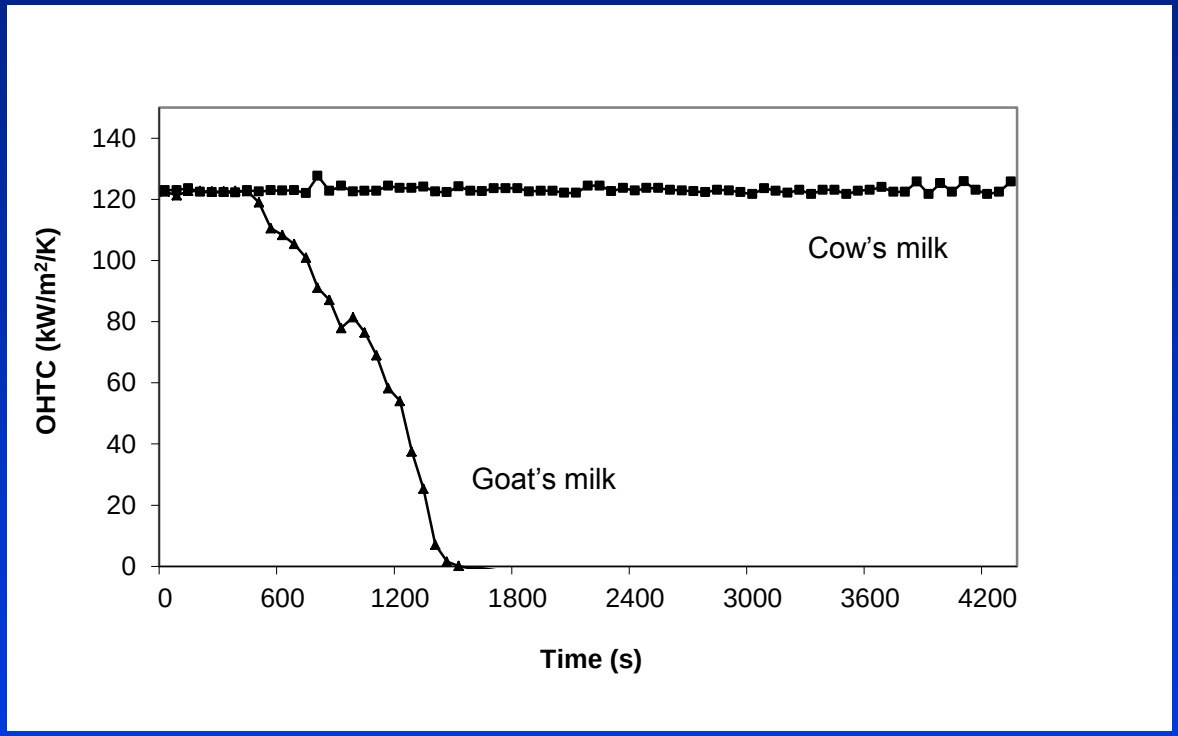
- High-temperature heating (e.g. UHT) of milk with high ionic calcium causes fouling of heat exchangers and sediment in the heated milk
- A classic example is goats milk; calcium chelating salts such as citrate or phosphates have to be added before UHT processing
- In some countries, citrate is added to all milk before UHT processing to minimise fouling

Fouling in UHT milk with added calcium chloride



Fouling of raw cow's milk with 0 mM (x), 0.7 mM (♦), 2.0 mM (■) and 3.4 mM (▲) added calcium chloride during processing at 135°C for 4 s *(Note: the lower the OHTC, the more fouling)*

Fouling of cow's and goat's milk during UHT processing



Calcium removal

Prevents rennet-induced coagulation

- Rennet coagulation occurs in two stages:
  - Proteolytic splitting of kappa-casein to *para*-κ-casein
  - Aggregation of the *para*-caseins into curd
- Step 1 does not require calcium
- Step 2 can only occur if ionic calcium is present
- Calcium chloride (~0.1%) is often added to milk during cheese making to enhance coagulation of step 2
- Conversely, coagulation of renneted milk can be prevented if the calcium is made unavailable (by removal or chelation) before the rennet is added
- Renneted, non-coagulated milk protein can be made into a powder and used to improve the body to cheese such as processed cheese if calcium is added back

Delays age gelation

- Age gelation occurs when UHT milk becomes viscous and forms a gel during storage
- It limits the shelf-life of UHT milk
- The role of calcium is unclear but:
- Addition of sodium hexametaphosphate (SHMP, polyphosphate, Calgon) which binds calcium greatly delays gelation
- Like rennet action – the 1st step is proteolysis and the 2nd step is curd/gel formation
- SHMP affects only the second step

Improves functional properties of milk protein concentrate

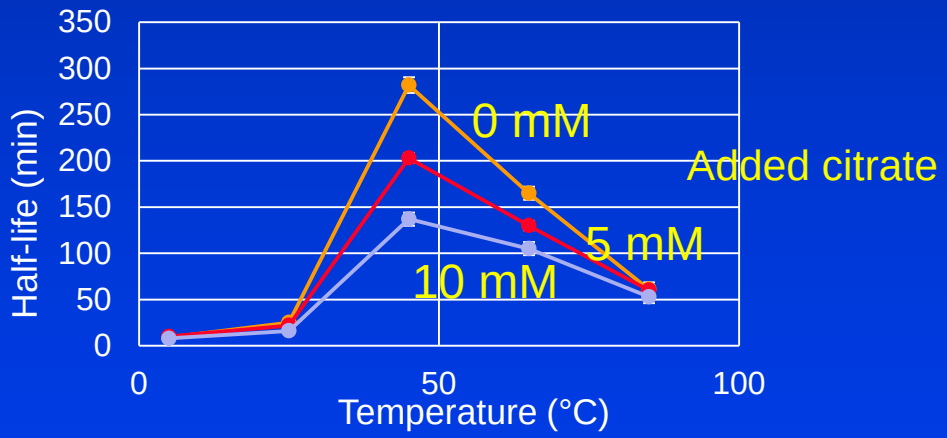
- Milk protein concentrate (MPC) is produced by membrane filtration of skim milk
- It contains all the proteins of milk – casein and whey proteins
- Protein concentration varies from 40 to 90%
- The ionic calcium level increases with protein concentration; MPC90 has ~ 5 mM Ca^{++} (cf milk at ~2 mM) and is unstable to heat.
- Removal of calcium by dialysis, ion exchange or adding chelating agents:
  - Markedly improves the heat stability
  - Improves emulsification properties
  - Improves solubility

Improves skim milk powder stability

- The heat stability of skim milk powder is important for several applications
- Can be improved by intense heating of the skim milk before evaporation and drying
- However, high-heat powders are not suitable for some applications
- Removing calcium by from skim milk before making medium- and low-heat powders improves its heat stability to in-container sterilisation
- Calcium can be reduced by adding chelating agents (phosphates, citrate) or ion exchange

Decreases foam stability

- Sometimes foaming is a problem and ways of reducing it are beneficial
  - For example, shaking reconstituted infant formula
- We found adding calcium chelating agents (citrate, SHMP, EDTA) reduces foam stability



Foam stability of reconstituted skim milk powder with added trisodium citrate (TSC)

Allows formation of iron-milk protein complexes

- Iron deficiency anaemia is one of the most widespread health disorders throughout the world
- Fortification of milk with iron may alleviate the problem
- Adding iron to milk is tricky as it causes oxidation and rancid flavours
- If calcium is removed from milk, e.g., by ion exchange, the casein micelle collapses (the glue, colloidal calcium phosphate, is removed) – skim milk loses opacity
- If iron, in the form of a salt like ferric chloride, is added, the iron binds strongly to the caseins
- The iron-protein complex can be made into a powder and added to foods to fortify them with iron
- NZ patent

Conclusions

- Calcium is an important nutrient in milk and milk products
- Calcium, particularly in the ionic form, binds strongly to milk proteins and is important for several functional properties
- Addition of calcium is sometimes desirable or essential – aids gelation, coagulation
- Removal of calcium is sometimes beneficial – prevents fouling, improves heat stability

References

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Thank you for your attention