



Co-precipitates, types, their specifications

- **Co-precipitate** of milk proteins is defined as product which separates as solid phase after heat treatment and precipitation of dairy fluid, or mixture of dairy fluids, which contain both casein and heat coagulable whey proteins.
- Resultant product contains significant proportion of whey proteins and almost all casein present in raw material.
- The term "Co-precipitates" as it covers combination of milk proteins as well as the proteins derived from other biological systems.
- Level of calcium in co-precipitate has major effect on its functional properties.
- Control of calcium level is achieved by varying amount of CaCl_2 added, changing length of time at which milk is held at about 90C and varying pH of precipitation by acid for low and high calcium co-precipitates.


- **Flexibility inherent in the co-precipitate process enables products to be produced, which vary in casein to whey protein ratio, solubility, ease of whipping, water binding, equilibrium moisture, viscosity and compatibility with other foodstuffs.**
- **Co-precipitates may be used as an ingredient in the preparation of various food products such as in dairy, meat, baked, confectionary, snack and animal and pet foods, to contribute desired functional properties or to improve nutritional qualities of products.**
- **Rich in proteins and low in lactose.**
- **Utilized for manufacture of foods and beverages for lactose intolerant people.**
- **Cost of production of co-precipitates is lower than that for skim milk powder and only slightly higher than that for casein.**

Muller et al., (1967) classified co-precipitates in three varieties:

**Low-calcium co –precipitate:
Calcium content in these co-precipitates is 0.5-0.8%**

A large, dark grey downward-pointing arrow with a white outline, indicating a flow from the first category to the second.

**Medium calcium co-precipitate:
Calcium content in these co-precipitates is 1.5%**

A large, dark grey downward-pointing arrow with a white outline, indicating a flow from the second category to the third.


**High calcium co –precipitate:
Calcium content in these co-precipitates is 2.5-3.0%**

Kozhev et al., (1970) classified co-precipitates:

Acid co-precipitates: Calcium content in these co-precipitates is 0.8-1.0%



Low calcium co-precipitates: Calcium content in these co-precipitates is 1.2-1.5%



Medium calcium co-precipitates: Calcium content in these co-precipitates is 2.0-2.5%



High calcium co-precipitates: Calcium content in these co-precipitates is 3.5-4.5%

Basic Principle.....

- **Following precipitation of caseins from skim milk by acidification or renneting, whey proteins remain soluble (in the whey).**
- **However, these can be precipitated in combination with the casein by first heating milk to such an extent that denature majority of the whey proteins and induce complexation of the whey proteins with casein, followed by precipitation of the milk protein complex by acidification to pH 4.6 or by a combination of added CaCl_2 and acidification.**
- **Precipitate of casein and whey proteins together from heated skim milk by acidification is termed as "co -precipitate".**
- **Co-precipitates of milk proteins are formed by a two -stage process:**
- **i) Heat treatment of milk or a mixture of products which provide casein and whey protein ii) Precipitation of proteins from the heated milk. The precipitated proteins then separated from serum, washed and dried.**

- **To obtain highest possible protein yield, it is necessary to heat milk before precipitation.**
- **Preheating to temperature above 65 C promotes interaction between β -lactoglobulin and κ -casein, thus leading to complex formation between whey protein and casein.**
- **Complexed whey protein will then co-precipitate along with casein after addition of precipitating agent.**
- **For maximum protein recovery, heating temperature had to be at least 85 C.**
- **Interaction between β -lactoglobulin and κ -casein changes the functional properties of caseins considerably.**
- **Co -precipitate is a total milk protein preparation with properties different from those of native protein fractions.**

- **Calcium conc. in co-precipitates can be maintained by changing basic parameters in production process: higher pH value at precipitation results in higher calcium concentration in the product, while longer retention time at high temperature decreases calcium concentration.**
- **CaCl₂ conc. of about 0.2% of skim milk quantity results in highest recovery of milk proteins (> 95%).**
- **Level of CaCl₂ required in milk for precipitation of high calcium co-precipitate is inversely related to precipitation temperature. At 90 C, conc. of 0.2% CaCl₂ in milk was required for complete precipitation, at lower temperature, it is necessary to use up to 0.3% CaCl₂.**

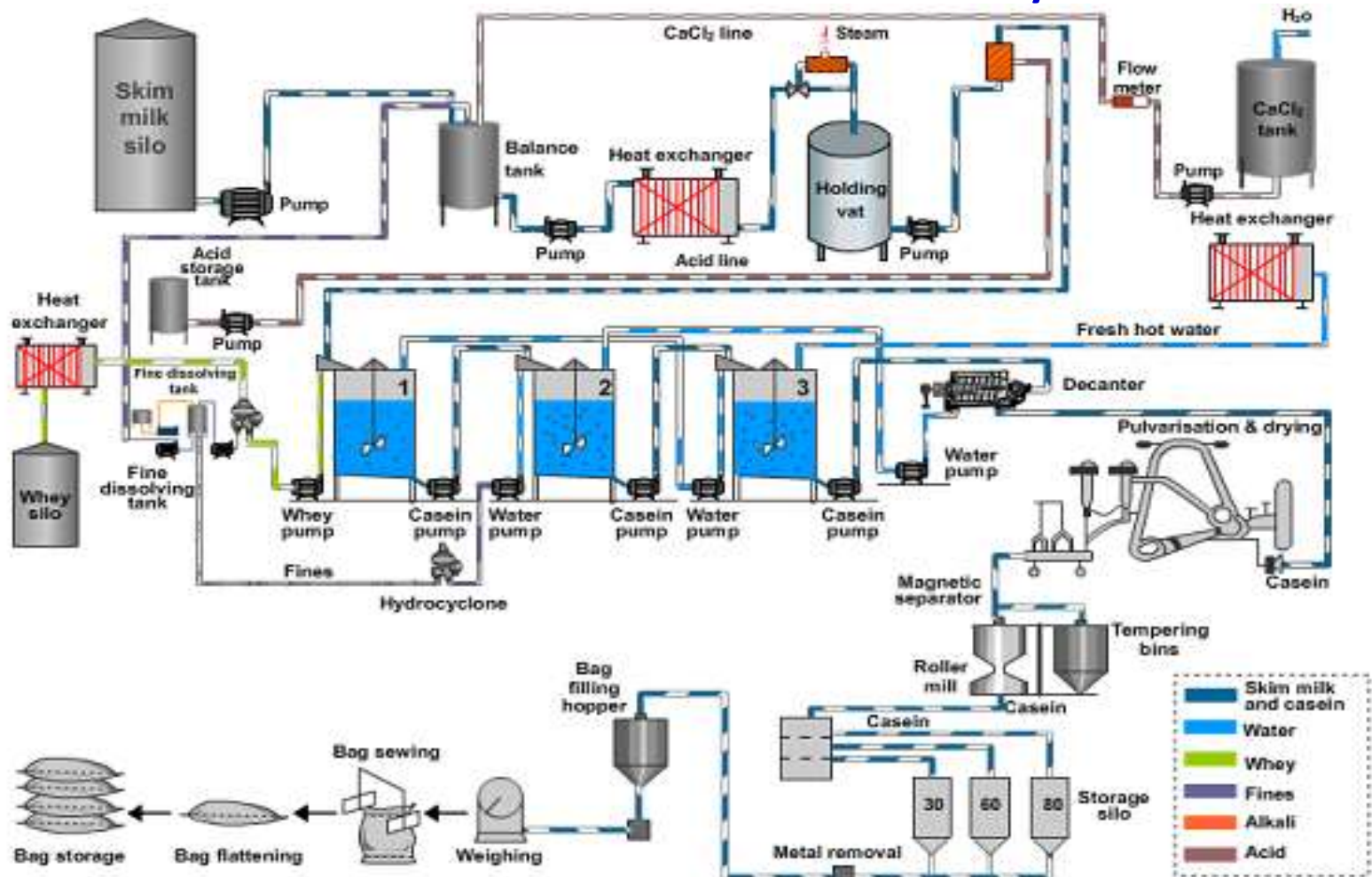
Manufacture of Co-precipitates

- **Early developments: USA and USSR.**

- **Co-precipitate manufacture was first reported in USSR in early 1950s, commercial potential of co precipitates was developed in 1960s and 1970s by research workers at Australian Commonwealth Scientific and Industrial Research Organization (CSIRO).**

Manufacturing Process.....

Type of plant used for casein manufacture can be adopted for manufacture of co-precipitates, by which it is possible to increase protein recovery from 80 -96% with a 28% reduction in B.O.D. of whey.



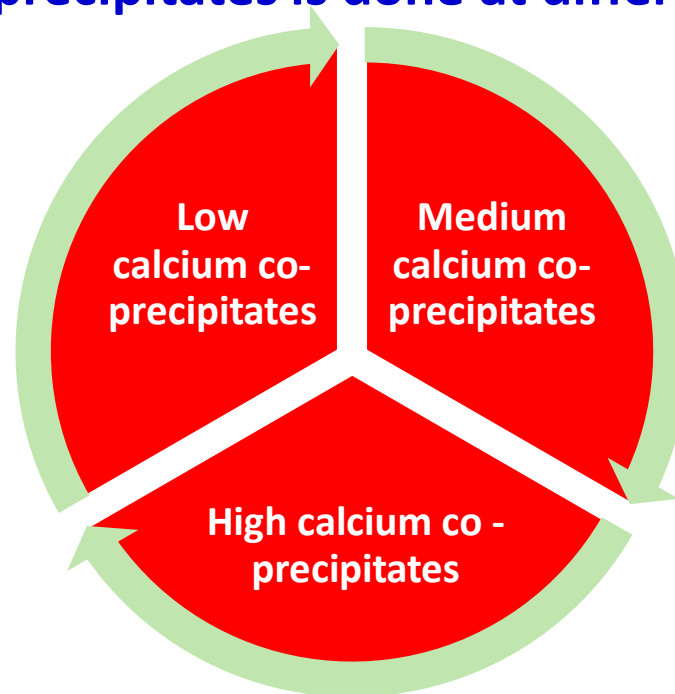
Continuous manufacturing plant for co-precipitates

Heating of buffalo skim milk.....

- Buffalo skim milk is heated in double jacketed stainless steel vat to 90.6 C by indirect heating or by direct steam injection.

Holding and precipitation

- Skim milk is held at varied holding times, depending on type of co - precipitate desired, at 90.6 C by maintaining temperature of hot water in the outer jacket at 93-94 C.
- Precipitation of co-precipitates is done at different pH ranges:



- **Low calcium co-precipitates.....**
- For low-calcium co-precipitate production, 0.03% of CaCl_2 is added to skim milk; the mix is then preheated to a temperature of 65-75 C by passage through a plate heat-exchanger.
- In next stage, final temperature of 90 C is obtained by steam injection into mix and this temperature is maintained for 15-20 mins in a holding vat.
- Two-stage heat treatment is employed for following reasons: (a) Plate - heat exchanger is to be used re-generatively in commercial operations and hence recovery of heat from whey is possible (b) If plate heat exchanger is only means of used for heating milk, there would be tendency for burn-on“ to occur in plates from slight precipitation of milk proteins, especially at temperatures above 68 C and at a pH of 6.3-6.5.

- After heat treatment, hot skim milk is cooled and then pH value is adjusted (pH 4.6) by injecting dilute hydrochloric acid (1:6) through spray counter currently to the direction of milk flow to provide full mixing. The mixture is transformed into curd in 20-25 secs in a holding tube.
- Precipitate is then separated from whey on an inclined 90-mesh screen, washed with water, pressed and dried.
- **Calcium concentration of low calcium co-precipitates: 0.1-0.5%.**
- In production of low calcium co-precipitates with calcium content of 0.5%, coagulation temperature 65 C produced slightly sticky and soft curd. Losses of fines in the whey are fairly high (about 1 ml/100ml, representing some 2% of co-precipitate), but are much lower in first wash water (approx. 0.1 ml/100 ml) which is usually heated to temperature near 40 C and maintained at a pH of about 4.6.
- Total fines losses amounts to approx. 2.5% of the low co -precipitate.

- **Medium calcium co-precipitates.....**
- **The same production process can result medium calcium co -precipitates (1.0-1.5% of calcium in the product) if 0.06% CaCl₂ is injected in the skim milk, and the mix is retained at a temperature of 90 C for 10-12 min and then precipitated at a pH value of 5.3.**
- **In the production of co-precipitates with calcium content of 1.0-1.5%, coagulation temperature of 65 C produced the firmest and most**
- **manageable curd.**
- **Most robust curd is precipitated at a pH of 5.2-5.3.**
- **When losses of fine curd particles are approx. 0.3 ml/100 ml in both whey and wash water, and accounted for about 2.1% of weight of co-precipitate.**

- **High calcium co-precipitates.....**
- For high-calcium co-precipitates production (2.5-3.0% of calcium in final product), skim milk is heated at 90°C and retained at this temperature for 1-2 min, then 0.2% CaCl₂ is added.
- Firmest high calcium co-precipitate curds and clearest whey are produced from milk heated at pH 6.4 and 85 C for 6 min, when
- 0.2% CaCl₂ is injected into hot milk and temperature of mixture is 77 C or higher.
- Fines in whey are reduced to level of 0.1 ml/100 ml or approx. 0.2% by weight of co-precipitate.
- When coagulation temperatures fell below 73 C, whey become cloudy and fine losses increased to 0.4 ml/100 ml or approx. 0.8% by weight of co-precipitate.

Drainage of whey.....

- After precipitation of co-precipitate curd, it is allowed to settle and whey removed after filtering through stainless steel strainer covered with muslin cloth. Filtration done to avoid loss of fine particles.

Washing.....

- Co-precipitate curd is given 2, 3 or 4 washings with acidulated water with 15 min holding time for each washing.
- **In low calcium co -precipitate**, curd is washed in water (up to four batch washes, each of 400-500 litre) at pH (pH 4.6) and at 45-55 C.
- **In medium calcium co -precipitate**, curd is washed, dewatered and dried as for low co -precipitate. Temperature of first wash water is 45-55 C and its pH is usually adjusted with dilute sulphuric acid to between 4.5 and 5.5 in order to assist in maintaining firm structure of curd. During this type of washing, properties of fine curd loses is reduced in each succeeding wash.

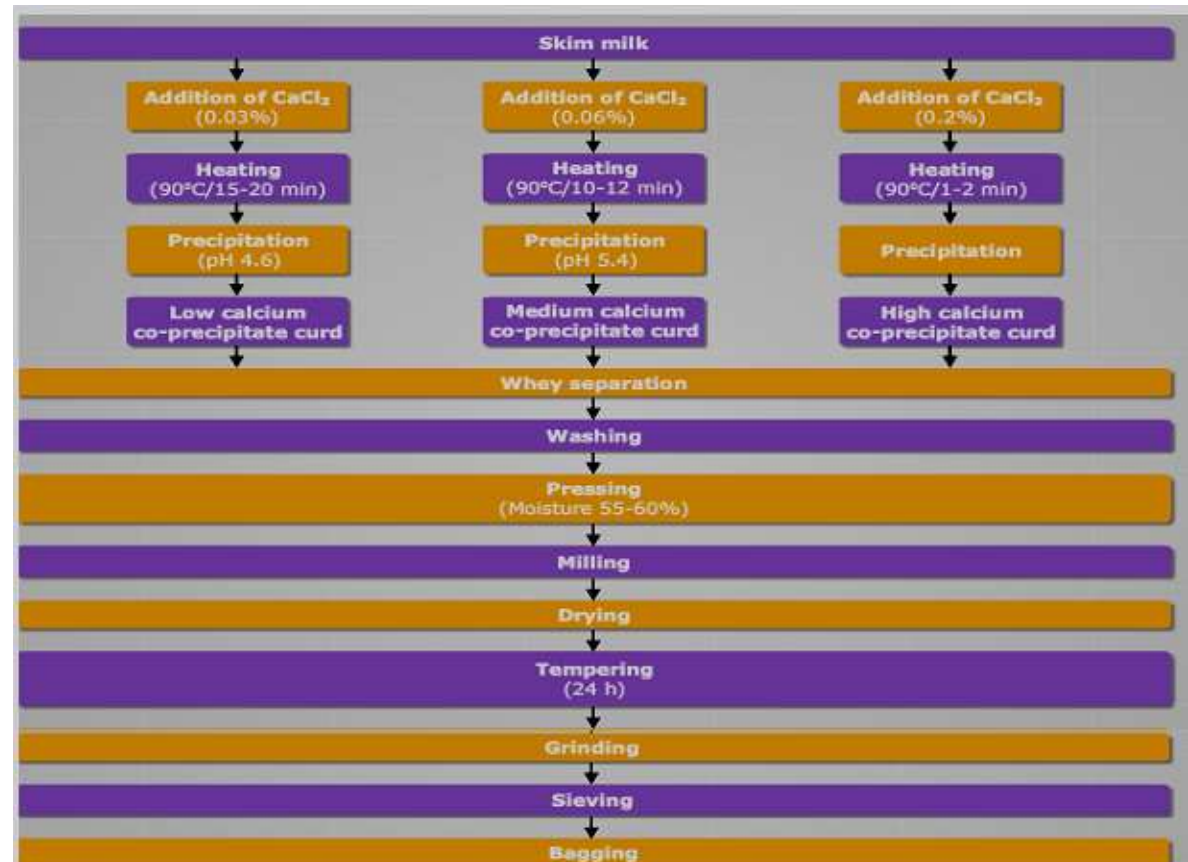
- **In high calcium co -precipitate**, when temperature of wash water is reduced to <60 C, curd becomes very soft and mushy with consistency similar to that of toothpaste. Wash water temperatures are therefore, adjusted to 60 –75 C for manufacturing of high calcium co -precipitates. Under these conditions, the losses of fine co precipitate particles in wash water, therefore any fines recovery amounted to approx. 0.5ml/100ml or about 2.5% by weight of co -precipitate. Combined fines losses from whey and wash water consequently represents about 2.7% by weight of high calcium co-precipitate. Wash water is acidified to pH 6.0 which is near pH of co-precipitate whey (pH 5.8-5.9).

Pressing.....

- **Pressing of curd is done with same principle as in casein. Curd can be subsequently de -watered using a decanter.**

Drying.....

- Co-precipitates is finally dried in granular form, to moisture content near 10% in pneumatic conveying ring drier.
- Typical drier has water evaporation capacity of approx. 3.5 kg/h using inlet and outlet temperatures of 190 C and 90 C respectively.
- After drying, co-precipitates goes for tempering, milling, blending, bagging and storage.

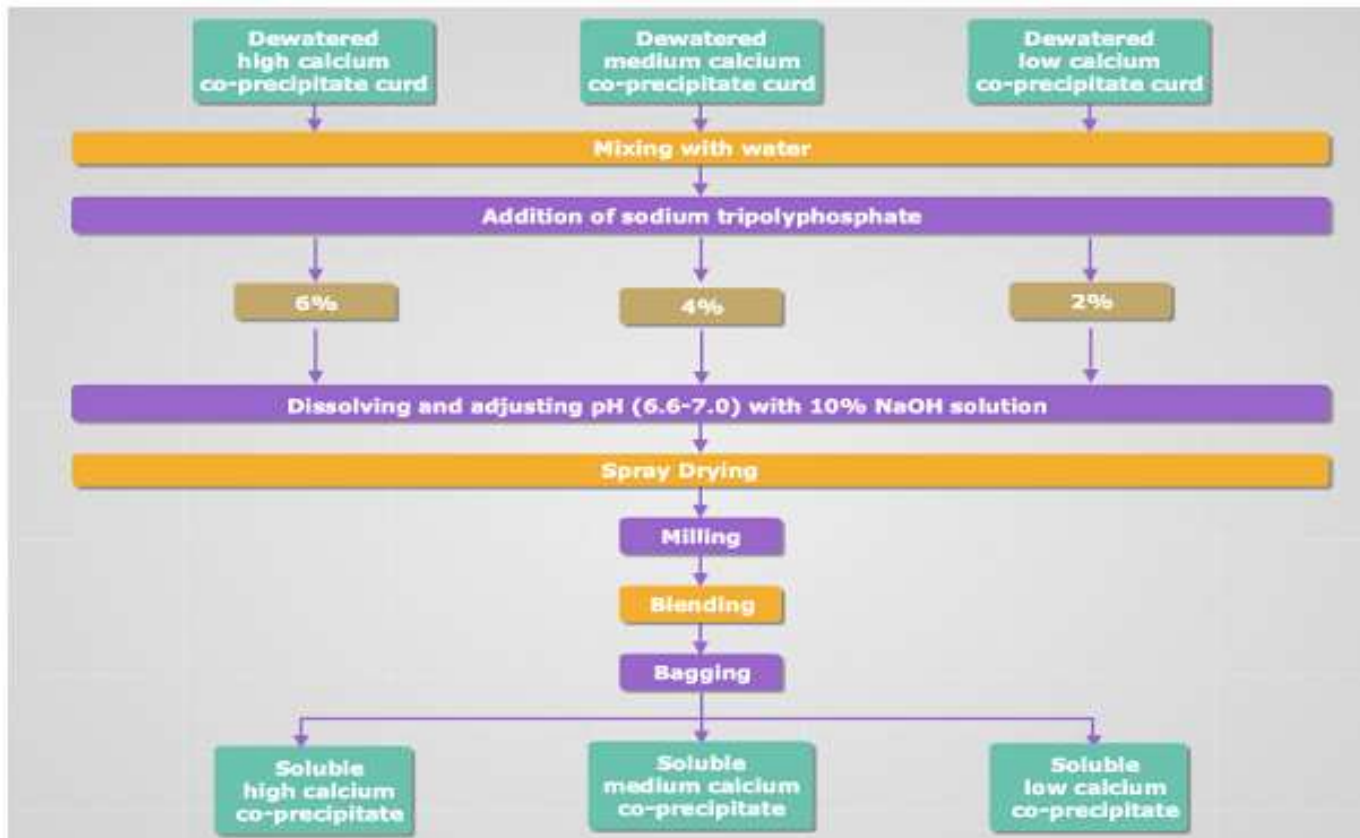


Manufacturing Process For Soluble Co-Precipitates

Flow diagram for production of low, medium and high calcium co-precipitates

- **Solubility of co-precipitates depends on calcium concentration in product.**
- **Up to 90% of low calcium co-precipitates are soluble in water at pH of 7.0, while high calcium co-precipitate is practically insoluble in water.**
- **In order to adequately dissolve medium calcium co-precipitate at neutral pH, sodium tripolyphosphate (calcium sequestering agent) can be added to mixture of co-precipitate and alkali.**
- **High calcium co-precipitate was dissolved at neutral pH by addition of sodium tripolyphosphate alone (6% on co-precipitate).**
- **For spray drying, wet curd of low, medium and high calcium co - precipitates are dispersed in water containing 2, 4 and 6 % sodium tripolyphosphate (STPP) respectively, calculated on dry weight basis of curd.**

- Mixture is heated in water bath (85 C) and continuous stirring is done for about 30 min.
- Slowly, 2.5 N NaOH solution is added to curd with constant stirring in such a way that pH do not rise to >7.0.
- Mixture is then passed through mini-pulveriser in place of colloid mill.
- Re-dispersed material is then filtered through muslin cloth.
- pH of dispersion is adjusted to 7.0 and material obtained is spray dried.



Flow diagram for production of soluble coprecipitates from dewatered coprecipitate curd