

Manufacture of sodium and calcium caseinates their physico-chemical and functional properties and food applications

- Soluble form of casein, caseinates may be prepared from freshly precipitated acid casein curd or from dry acid casein by reaction with dilute solution of alkali (sodium, potassium, calcium or ammonium hydroxide).
- For manufacture of caseinates, fresh acid casein curd is preferred over dry casein as raw material, since former yields caseinates with blander flavour.
- Caseinates prepared from dry casein will also incur additional manufacturing costs associated with drying, dry processing, bagging and storage of casein.
- Casein should have a low calcium content (< 0.15% dry basis) in order to produce caseinate solution with low viscosity and low lactose content (<0.2% dry basis) to produce sodium caseinate with best colour, flavour and nutritional value.
- Control of curd characteristics is important to ensure rapid dissolution.
- **Sodium caseinate** is most commonly used water soluble form of casein.

Manufacture of Sodium Caseinate

Formation of a casein suspension

A black downward-pointing arrow with a white outline, indicating the flow from the first step to the second.

Solubilization of casein using sodium hydroxide

A black downward-pointing arrow with a white outline, indicating the flow from the second step to the third.

Drying the sodium caseinate



Flow diagram for manufacture of sodium caseinate

Casein suspension and solubilization

- Fresh casein curd passed from a de-watering device (about 45% solids) is minced and finely-divided curd mixed with water at 40°C to give a solid content of 25-30% solids.**
- If dried casein is used, it is ground and held in water for sometime so that it absorbs water and becomes softened.**
- Casein suspension is then passed through colloid mill.**
- Temperature of emerging slurry, which may have consistency of 'toothpaste', should be below 45°C, since it has been observed that milled curd can re-agglomerate at higher temperatures.**

- **Main difficulties experienced in conversion of acid casein to sodium caseinate:**
 - (a) Very high viscosity of sodium caseinate solutions of moderate concentration, limits solids content for spray drying to 20%.**
 - (b) Formation of relatively impervious, jelly-like, viscous coating on surface of casein particles which hinders their dissolution on addition of alkali.**
- **To overcome former difficulty, pH and temperature are controlled during conversion as these influence viscosity, while latter can be overcome by reducing particle size by passing curd-water mixture through colloid mill prior to addition of alkali.**

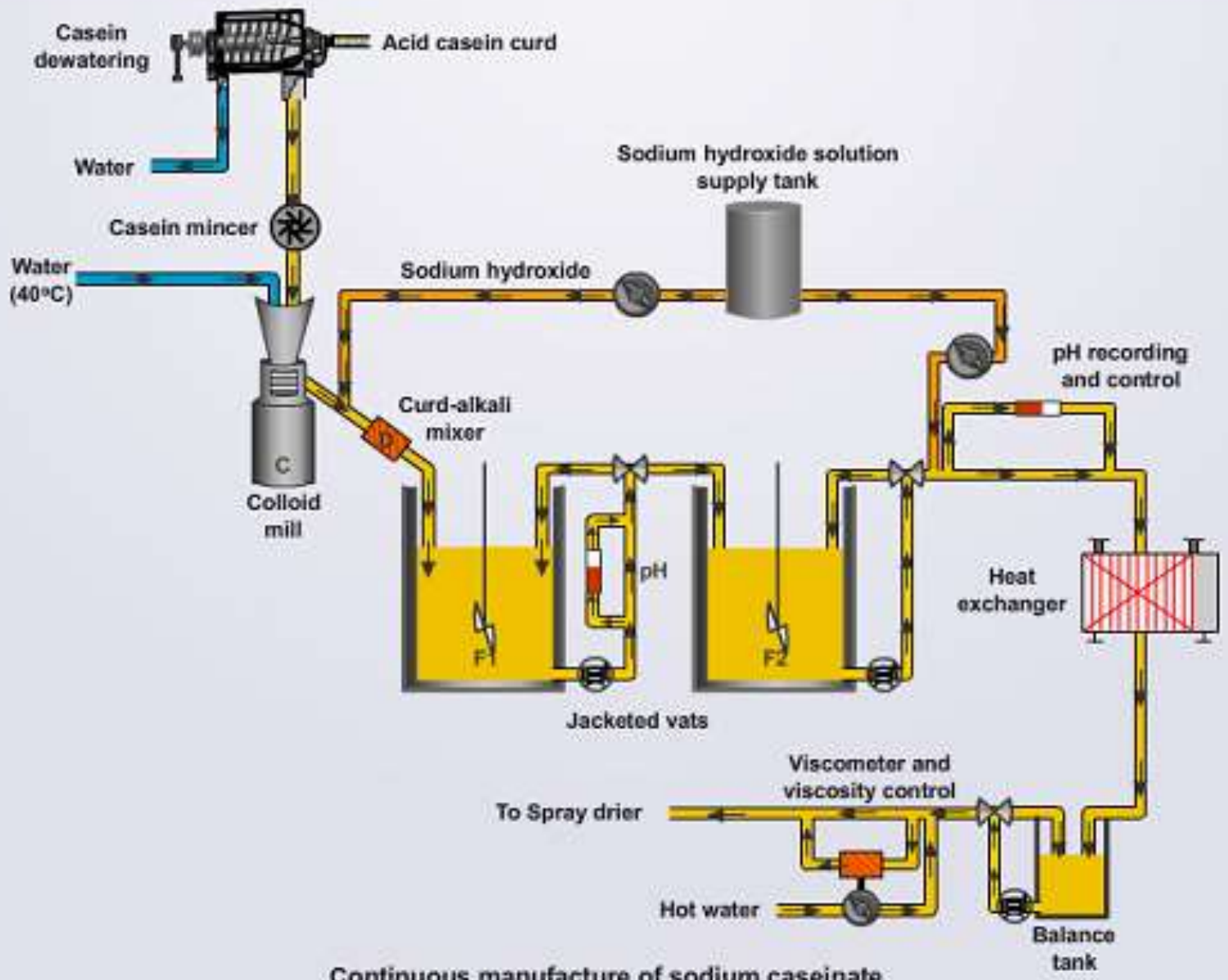
Addition of alkali and pH control

- NaOH solution with strength of 2.5 M is pumped into casein slurry, emerging with consistency of 'toothpaste' from colloid mill at 45 C.
- Quantity of NaOH required is generally 1.7-2.2% by weight of casein solids.
- Sodium bicarbonate/sodium phosphates may be used in manufacture of special citrated caseinates (cost is higher).
- Addition of dilute alkali must be carefully controlled with aim of reaching final caseinate pH of 6.6-7.0 (generally about 6.7).
- To achieve correct caseinate pH, add sufficient alkali to bring pH close to, but below specified value and then add additional alkali needed towards end of dissolving operation.
- This technique is used for following main reasons: **firstly, because reduction of pH of sodium caseinate solution by addition of acid is likely to cause localized precipitation of casein and secondly, development of any off-flavours associated with localized conditions of high alkalinity is minimized. Thirdly, potential for formation of lysinolamine when pH is excessively high (e.g. >10).**

Dissolving

- Casein alkali mixture is transferred to first dissolving vat, where it is recirculated and/or pumped to second dissolving vat where solubilisation is completed as the solution temperature is raised to about 75°C.
- An in-line pH meter is used to monitor and regulate addition of NaOH solution.
- Viscosity of sodium caseinate solutions is a logarithmic function of the total solid concentration.
- Each dissolving vat, therefore, must be equipped with a powerful agitator and a high speed recirculating pump.
- In addition to concentration, other factors which affect viscosity of sodium caseinate solutions are temperature (semi-logarithmic), pH, calcium content of the curd, type of alkali used and seasonal and genetic factors.
- The solution temperature is raised as quickly as possible to 60-75°C to reduce viscosity.

- **Care should be taken to avoid holding hot ($>70^{\circ}\text{C}$) concentrated sodium caseinate solution for extended periods prior to drying, since it is possible for brown colour to develop in solution due to reaction between protein and residual lactose.**
- **During dissolving operation, incorporation of air should be kept to a minimum since caseinate solutions form very stable foams.**
- **All joints on pipes, especially on suction side of pumps, must be airtight and recirculation line must discharge below surface of liquid in dissolving vat.**



Continuous manufacture of sodium caseinate

Drying of sodium caseinate solution

- Homogeneous sodium caseinate solution is usually spray dried in a stream of hot air.
- In order to ensure efficient atomization of sodium caseinate solution, it must have a constant viscosity as it is fed to the drier.
- It is common practice to minimize viscosity by preheating solution to temperature of 90-95°C just prior to spray drying.
- Minimize time for which caseinate solution is at high temperature.
- Total solid content of solution destined for spray drying ranges between 20 and 22% and only occasionally may be as high as 25%.
- At about 20% solid concentration of sodium caseinate solution, approx. 4 kg of water need to be evaporated to produce 1 kg of powder.
- Increase inlet air temperature to increase water evaporation rate.
- Steam radiators may produce inlet air temperatures of up to 170°C and indirect oil heating or direct gas firing produce inlet air temperatures of up to 260°C.

- **Warm spray dried sodium caseinate powder is cooled in fluid bed drier.**
- **Low solids content of feed solution produces spray-dried powder with low bulk density.**
- **Pressure nozzle dryers, operating at 100-250 bar, produce caseinate with higher bulk density than that from disc atomizing dryers.**
- **Powder particles produced on disc dryers tend get shape of hollow spheres.**
- **Since powder is so light, losses from product recovery cyclones may be rather high, so install bag filters for improved recovery.**

Alternative method of sodium caseinate drying

- Production of roller dried sodium caseinate by feeding mixture of curd (50-65% moisture) and an alkaline sodium salt (Na_2CO_3 or NaHCO_3) onto drying drum of roller-drier. Sodium caseinate with good flavour and high bulk density could be produced by using roller drier at relatively low steam pressure (low drying temperature).
- Production of granular sodium caseinate by lowering moisture content of acid casein curd to <40%, reacting curd with Na_2CO_3 with agitation for up to 60 min and drying resultant caseinate in a pneumatic ring drier/fluidized bed drier. Resulting caseinate has higher bulk density and improved dispersibility compared to spray and roller dried product.

- **Spray drying sodium caseinate solutions of higher solids content (up to 30%) in a drier fitted with modified atomizer disc/preparation of concentrated caseinate solutions (33-47% solids) by modified procedure and drying these solutions in spray/roller dryers/extrusion drying method.**
- **Conversion of casein to caseinate in presence of limited amount of water using extrusion technique. Commercially, casein in powder form is introduced and transported with water continuously into an extruder machine. An alkaline reagent is introduced in second step and whole mixture subjected to intense kneading under pressure with rise in temperature to initiate chemical reaction between casein and alkaline reagent. Mixture is subjected to second intense kneading under pressure and intense shear to finish off chemical reaction with temperature of mixture rising to cause mixture to melt and to obtain viscous caseinate paste. Then cooled with degassing operation to reduce and adjust its temperature and viscosity. Finally caseinate paste is extruded at 70-90°C with 30-40% moisture to form continuous strand of caseinate paste at outlet from extruder machine. Continuous thin sheet of caseinate paste is formed from strand. Sheet of caseinate is simultaneously cooled below 20°C and cut longitudinally into plurality of parallel strips.**

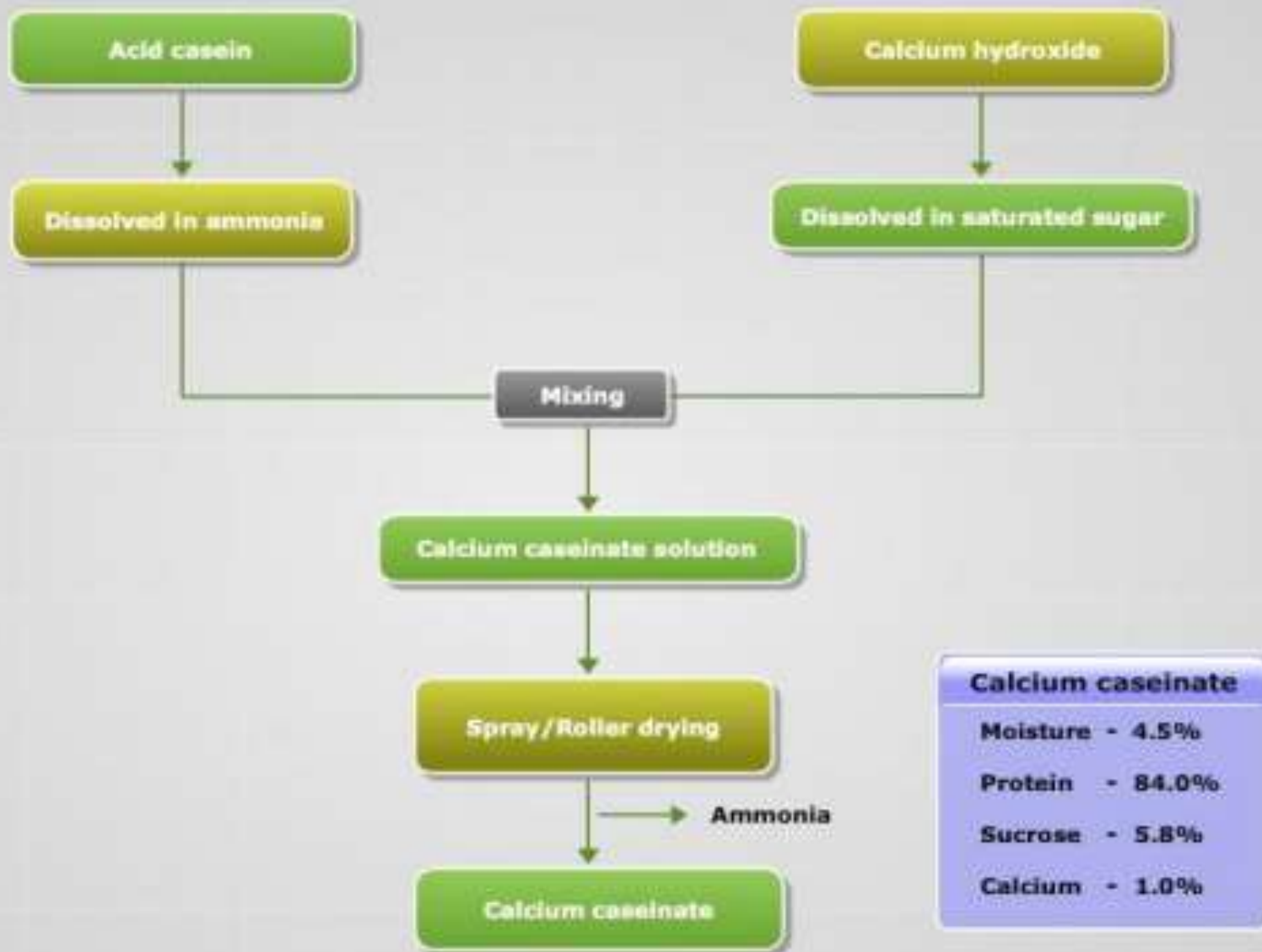
Calcium Caseinate

- Finds use in both pharmaceutical preparations and as a food ingredient.
- Various countries have prescribed varying specifications for caseinates.
- In contrast to translucent, viscous, straw-coloured sodium, potassium and ammonium caseinate solutions, calcium caseinate forms micelles in water, producing an intensely white, opaque, 'milky' solution of relatively low viscosity.
- Calcium caseinates are much less soluble and have poorer functional attributes than sodium caseinate.



Manufacture of Calcium Caseinate

- **Calcium caseinate solution is destabilized on heating especially at pH values below 6.**
- **During the dissolving process, reaction between acid casein curd and calcium hydroxide (the alkali most commonly used in the production of calcium caseinate) proceeds at a much slower rate than that between curd and sodium hydroxide.**
- **Temperature of conversion is a particularly important factor in determining completeness of solubility (assessed from the amount of sedimentable matter) of calcium caseinate. Therefore, dissolving process must be closely monitored to ensure production of calcium caseinate with a good solubility.**



Flow diagram for production of calcium caseinate

- **Calcium hydroxide is soluble in sugar solutions and may, therefore, be used in this form for reaction with acid casein.**
- **In order to increase rate of reaction between casein and calcium hydroxide, casein may first be dissolved completely (and rapidly) in ammonia.**
- **Calcium hydroxide solution of sugars (sucrose, glucose, galactose, lactose or fructose) is then added and solution of calcium caseinate dried by means of roller drier.**
- **Ammonia evaporates during processing, leaving relatively pure calcium caseinate (protein 84%, sucrose 5.8%, moisture 4.5%, calcium 1.0%) with nutritional properties similar to those of original casein.**

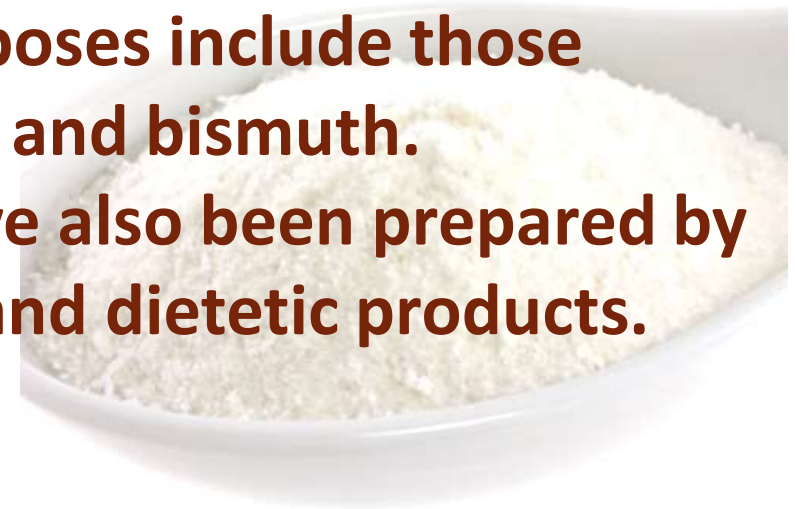


Ammonium/Potassium/Citrated Caseinates

- **Ammonium and potassium caseinates** may be prepared by a method similar to that used for production of sodium caseinate by substituting NH_4OH or KOH for NaOH .
- **Granular ammonium caseinate** may be prepared by exposing dry acid casein to ammonia gas and removing excess ammonia with stream of air in a fluidized bed degassing system.
- **Citrated caseinate** has been prepared similar to that used for preparation of spray dried sodium caseinate by using mixture of trisodium citrate and tripotassium citrate in place of NaOH .

Other Caseinates

- **Magnesium caseinate** is prepared from casein and a magnesium base or basic salt such as magnesium oxide, magnesium hydroxide, carbonate or phosphate or by ion exchange.
- Compounds of casein with aluminium may be prepared for medicinal use or for use as an emulsifier in meat products.
- Heavy metal derivatives of casein have been used principally for therapeutic purposes include those containing silver, mercury, iron and bismuth.
- **Iron and copper caseinates** have also been prepared by ion exchange for use in infant and dietetic products.



Specifications of Caseinates

Requirements	Caseinate
Moisture	Not more than 8.0 percent m/m
Milk Fat	Not more than 2.0 percent m/m
Milk Protein (Nx6.38) on dry weight	Not less than 88.0 percent m/m
Casein in Protein	Not less than 95.0 percent m/m
Lactose	Not more than 1.0 percent m/m
pH Value in 10% solution	Not more than 8.0

FSSAI (2011) compositional standards for edible sodium caseinate

- As per FSSAI (2011), edible caseinate means dry product obtained by reaction of edible casein or fresh casein curd with food grade neutralizing agents and which have been subjected to an appropriate heat treatment.
- Product shall be white to pale cream or have greenish tinge; free from lumps and any unpleasant foreign flavour.
- May contain food additives permitted in these regulations.

Composition	Sodium caseinate	Calcium caseinate
Moisture (%)	3.8	3.8
Protein (N x 6.38) (%)	91.4	91.2
Ash (%)	3.6	3.8
Lactose (%)	0.1	0.1
Fat (%)	1.1	1.1
Sodium (%)	1.2 -1.4	< 0.1
Calcium (%)	0.1	1.3-1.6
Iron (mg/kg)	3-20	10-40
Copper (mg/kg)	1-2	1-2
Lead (mg/kg)	<1	<1
pH	6.5-6.9	6.8-7.0

Typical composition of caseinates

Within general pH range of 6.5-7.0, sodium caseinate will usually contain 1.2-1.4% sodium, while calcium content of calcium caseinate is generally in range 1.3-1.6%.