

A white plate containing a white powder, likely whey powder, is shown on a textured, light-colored surface. The powder is piled on the plate and has spilled slightly onto the surface around it. The background is a mottled, light brown and beige color with a fine, grainy texture.

# **Deproteinized and Demineralized Whey**

**High level of minerals (0.7-0.8%) present in whey restricts their commercial utilization. Whey based products have salty flavour owing to high mineral content. Whey is demineralised to produce dry demineralised whey. Processes that have been utilized for demineralisation of whey include electro dialysis, ion exchange, and loose reverse osmosis. These processes do not denature proteins, thereby preserving protein solubility in demineralised whey. Demineralised whey will have less salty flavor because of removal of minerals.**

# Utilization of Demineralised Whey

**As ingredients in infant formulae**

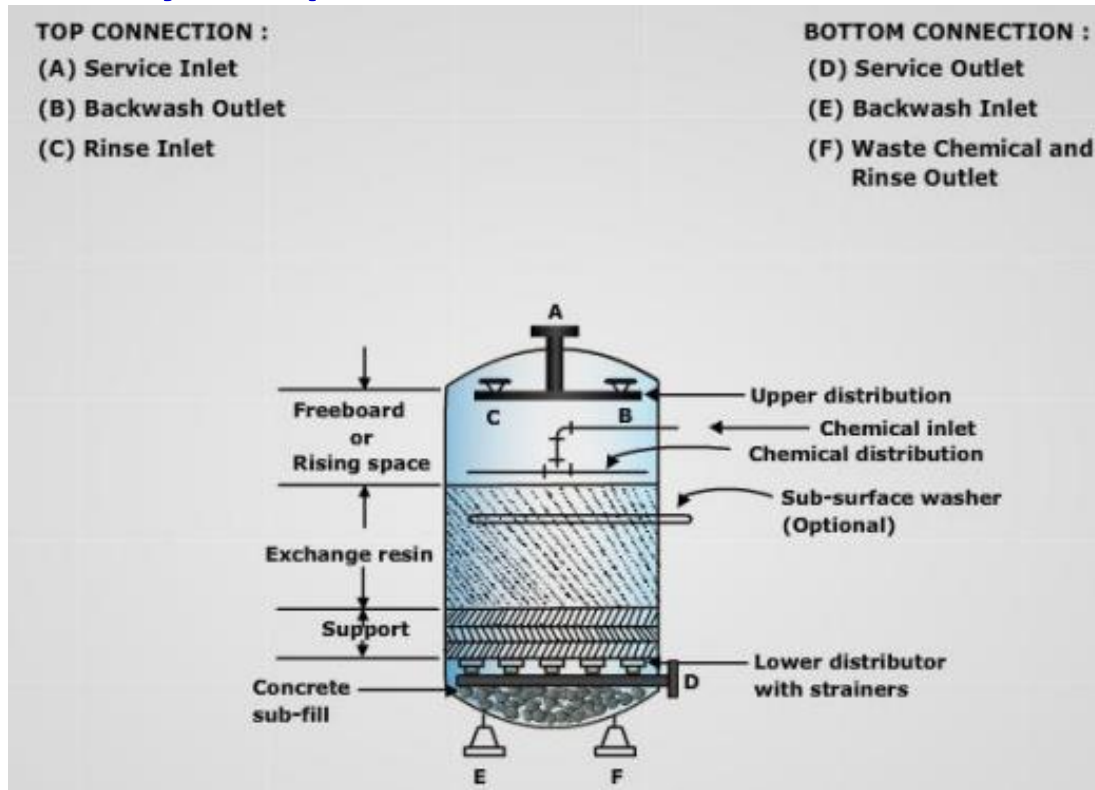
**Production of demineralised calf milk replacers**

**Dietetic food, coffee whi tener, soft serve ice-cream, milk shakes, whey drinks, citrus drinks, salad dressing, animal feeds, baker goods, confectionary coating and dry mixes**

**Less expensive substitute for non fat dry milk**

**Cottage cheese whey is demineralised to reduce effluent costs**

- Ion exchange: Demineralisation technologies, fixed-bed technique involving use of resins which have a discrete capacity for absorption of minerals. When this capacity is used up, absorbed minerals have to be removed from resin and resin regenerated, before it can be used again.
- Widely used for whey demineralisation.
- **Disadvantages:** Potential denaturation of protein due to low pH in cation column and loss of protein in anion column that makes product less widely accepted for use in infant formula.



**Ion Exchange Resin**

- ❑ Modern ion exchange resins are macro-molecular porous plastic materials formed into beads with diameter in range of 0.4-0.8 mm having large number of attached bonds on their surface which can absorb one specific type of ions.
- ❑ Chemically, they act as insoluble acids or bases, which when converted into salts, remain insoluble.
- ❑ Average pore size within polymer is normally less than 40 Å.
- ❑ Macro porous resins are prepared by re-dissolving part of matrix of polymer to controlled pore sizes up to 1000 Å.
- ❑ Matrix of resin contains charged sites involved in ion exchange process.

#### Resin matrix materials

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Silicates - inorganic cellulose base		Cross-linking agent, e.g.
Phenol formaldehyde		divinyl benzene (DVB)
Polystyrene		
Polyacrylate		

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Charge type	Affinity level	Functional group
Cation exchange resin	Strong acid	SO <sub>3</sub> <sup>-</sup> sulphonate
	Weak acid	COO <sup>-</sup> carboxyl
Anion exchange resin	Strong base	NR <sub>3</sub> <sup>+</sup> quaternary ammonium
	Weak base	NH <sub>2</sub> .HNR, NR <sub>2</sub> substituted amino groups

### Classification of ion exchange resins

### Ion affinities for different exchange resin group

Resin group	Affinity series
Strong acid cation	Fe <sup>3+</sup> > Al <sup>3+</sup> > Ca <sup>2+</sup> > Mg <sup>2+</sup> > K <sup>+</sup> > Na <sup>+</sup> > H <sup>+</sup>
Weak acid cation	H <sup>+</sup> > Fe <sup>3+</sup> > Ca <sup>2+</sup> > K <sup>+</sup> > Na <sup>+</sup>
Strong base anion	SO <sub>2</sub> > <u>Cl</u> > CH <sub>3</sub> COO <sup>-</sup> > OH <sup>-</sup> > HSO <sub>3</sub> <sup>-</sup>
Weak base anion	OH <sup>-</sup> > SO <sub>4</sub> <sup>2-</sup> > CH <sub>3</sub> COO <sup>-</sup> > HCO <sub>3</sub> <sup>-</sup>

## **Processing Variables**

**Both degree of demineralization and feed condition and type of whey and permeate must be considered during demineralization of whey and ultrafiltration permeates.**

### **Degree of demineralization:**

- Levels of up to 95% demineralization of whey-based fluids can be achieved by ion exchange.**
- Required level of demineralization is achieved by operating ion exchange plant at constant flow rate and high degree of demineralization, and by using varying amounts of bypass to achieve desired level of demineralization in end product.**
- Ion exchange is generally non selective with respect to ions removed.**
- Bypassing does not result in significant change in distribution of various minerals present in end product. Reduce losses of protein and lactose.**

## **Feed condition and type:**

- **Physical condition of whey feedstock is an important factor determining efficiency and effectiveness of ion exchange processes.**
- **Most problems are caused by inadequate removal of agglomerates prior to ion exchange.**
- **These agglomerates may be casein or cheese curd fines, or may be produced by pretreatments of feedstock (heat treatment).**
- **There are often benefits by increasing concentration of feedstock prior to ion exchange.**
- **Whilst concentration reduces volume to be processed, it does not reduce demineralization load.**
- **As concentration of solution increases, selectivity of ion exchange system generally moves towards monovalents.**
- **Increased concentration of non-ash components may also lead to increased losses of these components eg., increased protein absorption by resin.**
- **Source of whey (sweet or acid) does not influence mineral profile of dematerialized product, though demineralization load is higher for acid whey.**



## **Temperature of operation:**

- **Temperature at which demineralization is carried out is often dictated by matters not related to actual demineralization process.**
- **Maximum temperatures of operation for resins vary from 35-50 C for strong base resins, 60-100 C for weak base, to 120 and 150 C for weak and strong acid resins, respectively.**
- **Use of lower temperatures will reduce extent of losses of protein and lactose by resin absorption, and assist in prevention of microbial growth in system during long loading phase.**
- **Temperatures of 10 C are often employed for these reasons.**
- **Extent of protein losses, and thus reduced yield, can be very significant as temperature rises.**

# Operating Problems

## Physical:

- Resin beads are physically fragile, but often are subjected to considerable stress in operation.
- Bead fracture and attrition is common, and can be caused by effects of changing of processing parameters during various cycles of loading, backwashing, regeneration and rinsing.
- Change in type of solutions to which resins are exposed during these cycles also subjects them to osmotic shocks.
- Resin may be subjected to stress owing to pumping operation and temperature changes.

## **Chemical:**

- **Chemical fouling of resins is most common problem encountered in ion exchange processing.**
- **Feedstock, whey or permeate contains many organic substances in low concentrations.**
- **These may enter feedstock through milk, or from sanitizers used on farm and in plant operations such as cheese- or casein-making.**
- **Foulants can also enter system from regenerants, and via wash or rinse waters. Such foulants include tannic, humic and fulvic acids.**
- **Fouling by organic compounds occurs mostly on anionic resins; fouling by inorganic compounds occurs most commonly on cationic resins.**
- **Fouling by organic molecules can be the result of their very slow diffusion through the resin matrix, because of their large size.**

- **Irreversible bonding can also occur if there is a high selectivity for sites.**
- **Strongly basic anion exchange resins cross-linked with acrylic derivatives rather than divinyl-benzene is less susceptible to fouling.**
- **Fouling by inorganic ions cationic resins is generally caused by iron, manganese and copper.**
- **Precipitates, such as calcium sulphate, can cause surface fouling and scaling of resins.**

## **Non mineral losses:**

- **Protein losses, owing to factors other than temperature and pre-treatment history, have been reported to occur on demineralisation by ion exchange.**
- **Significant losses of non-protein nitrogen (NPN) can also occur.**
- **Losses of 50-70% of NPN have been reported on demineralization of cheddar cheese whey with strong acidic and weak basic resins.**

## **Structural leakages:**

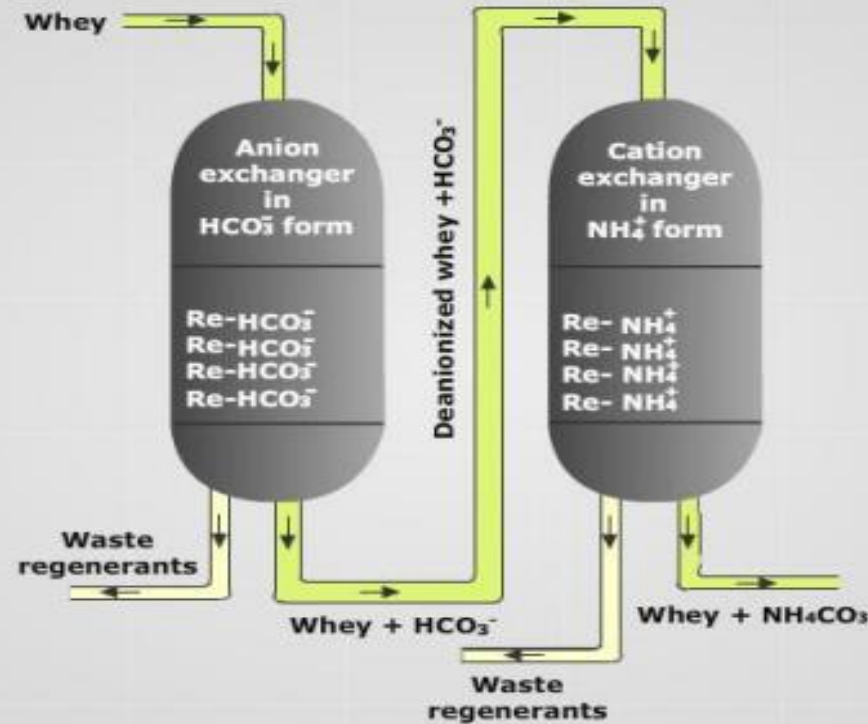
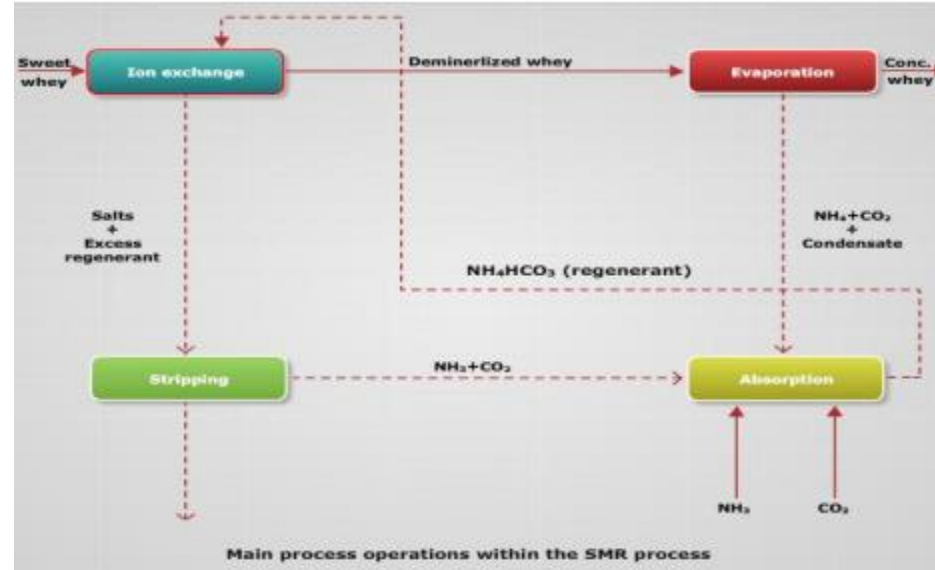
- **Possibility of slow leakage of organic material from resin structure during its life of operation is a cause for concern.**
- **Styrene monomer, which may be present in bead from incomplete polymerization, will slowly leave the bead during its service life.**

# Process Variations

## SMR process:

- A variant of traditional ion exchange process is Swedish SMR (Svenska Mejeriernas Riksferening or Swedish Dairy Association) process.
- Designed primary to reduce consumption of regeneration chemicals, which apart from saving money, also leads to better waste (reduced salt load) situation from demineralization plant.
- Instead of using cation resin of  $H^+$  form and anion resin on  $OH$  form, this process uses cation resin on  $NH_4^+$  form and anion resin on  $HCO_3^-$  form.
- System has two major innovations; first order in which ions are exchanged is reversed from that commonly employed – anions are exchanged first, and cations second; secondly, separate regenerants are replaced by solution of one salt.
- Both ions in this single regenerant solution are used, one for each of anion and cation exchange columns.

- SMR process reduce high consumption of chemicals and water normally associated with ion exchange processes during regeneration.
- Reduce associated water disposal problems and their cost.
- Process does not result in such wide changes in pH of feedstock during demineralization as in normal ion exchange.
- During normal ion exchange, decationised whey reaches at pH of 1.5 and on deanionisation, pH of product may increase to 9 or 10.
- For sweet whey, SMR process restricts pH variation between 6.5 and 8.2.



Ion exchange reaction in SMR process

## **Thermal regeneration:**

- **Use of thermal processing for regeneration of resins can reduce both chemical and effluent processing costs.**
- **A range of such products, known as Sirotherm resins, are now commercially available.**
- **Mild heat treatment results in regeneration of these resins.**



## **Electrodialysis Process**

- **Gap between ED membrane is very small (0.4-1 mm), so whey is clarified before processing otherwise deposits will be formed varying level of demineralisation.**
- **Pre-concentration, acidification and decalcification can also affects demineralisation.**
- **Manufacture of demineralized whey by electro dialysis begins with pasteurization of whey and concentration to around 28% TS.**
- **Concentrated whey is clarified to remove any insoluble protein and fines and then passed through ED stack.**
- **Typical structure with 100 pairs of cells represents a space of 50  $\mu\text{m}$  and can remove 60% of salts from 25% whey concentrate at flow rate of 500 l/h.**

- Ions removed by electrodialysis are  $\text{Na}^+$  and  $\text{K}^+$ .
- Calcium, magnesium phosphate and citrates are not transported as they are probably present, at pH value of electrodialysis, in form of soluble complexes.
- Ions of different charges and sizes have quite different mobilities, and hence, removal of ions from whey by electrodialysis is not uniform, depending in particular on ionic composition, mode of operation and contact time.
- Multivalent ions are only removed after monovalents are essentially removed.
- Level of demineralization is determined by initial ash content, whey viscosity, current density and residence time.
- Electrodialysis is used where low levels of demineralization are sufficient, since power consumption at high level of demineralization is excessive.

- **Batch operation** is quite convenient when a high and uniform level of demineralization is required (90% whey demineralization for infant formulations).
- Process times of 3.5-6 h are typical, depending on operating temperature (35-45 C), that provides maximal electric conductivity, degree of demineralization etc.
- For 90% demineralization, holding in batch system can be as long as 5-6 h at 30-40°C.
- Pre-concentration of whey to 20-30% DM is desirable for better capacity utilization and lower electrical power consumption.
- Lower temperatures (20 C) and feed concentrations (even 12% TS) may be used, but higher voltage is required to provide corresponding current density.

- **In continuous operation, whey flows through number of electro dialysis stacks in series with partial flow recirculation through individual stacks.**
- **Operation temperature is relatively low (as low as 20°C) and pH remains constant (about 4.7) during processing.**
- **Whey at 6% TS can be processed with no pre-concentration.**
- **Continuous electro dialysis has longer period of uninterrupted operation (10-12 h) than batch wise processing, convenient for large-scale production.**
- **Conductivity, pH and temperature of whey and brine streams are monitored continuously.**

- **Losses of non mineral components occur in electro dialysis.**
- **Loss in product yield.**
- **Loss of lactose and proteins is undesirable.**
- **Losses usually occur at higher level of demineralization.**
- **NPN losses are about 25% and lactose losses of about 6% occur on 90% demineralization.**
- **Physical losses may also occur due to leakage at gaskets.**
- **After demineralisation, whey is usually further concentrated by evaporation to about 55% solids and spray dried.**

## **Ion Exchange**

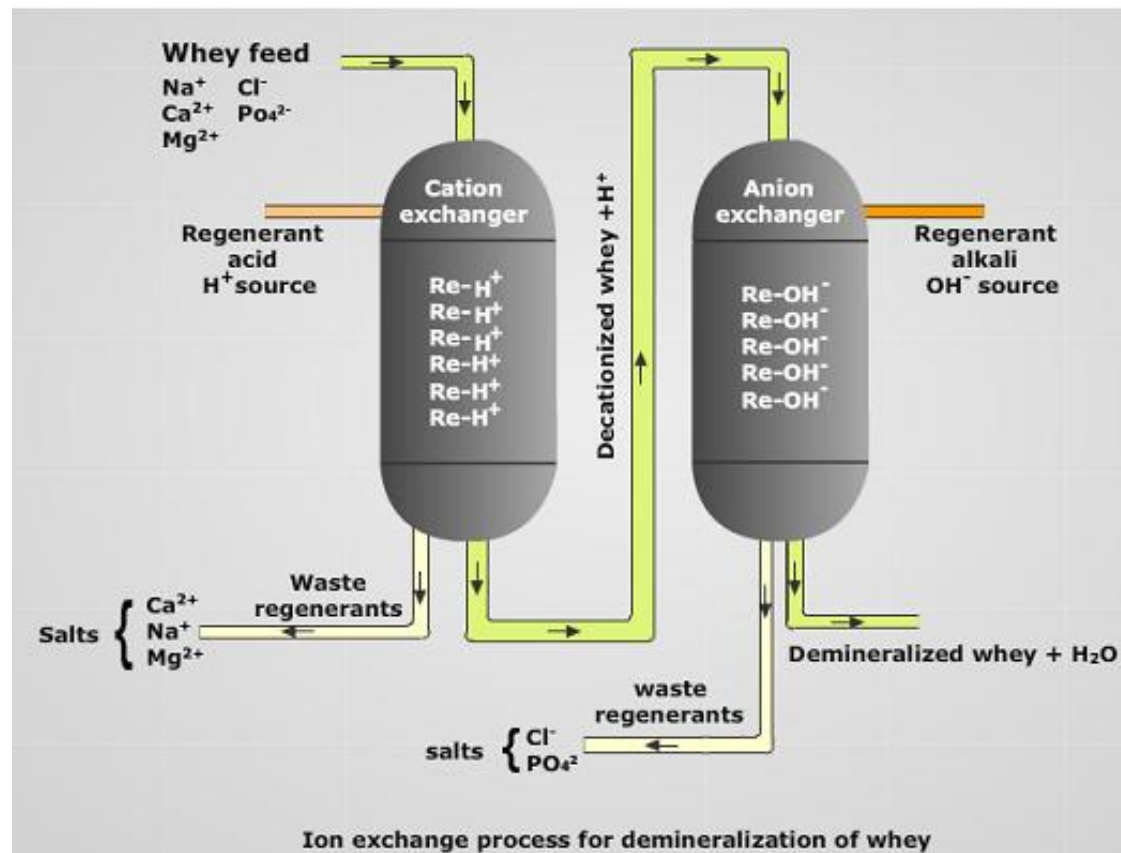
- **Ion exchange processing of whey is based on ability of macromolecular resins to exchange their surface-bound ions for mobile ions of same charge from treated whey.**
- **Whey processing is best carried out using strong acid cation and medium to weak base anion resins.**
- **Column systems are employed for practical demineralization of whey.**
- **In such systems, either each resin is packed into its own column, or alternatively, sometimes, resins are used in a 'mixed bed' column.**
- **Simplest system is a continuously -stirred reactor tank.**
- **Before demineralization, whey has to be pasteurized, clarified and separated, because contamination of resin with fat, and/or fine cheese curd, results in shortening of production life of resins.**

- **Whey pasteurization should be as mild as possible (65°C, 15 sec), since any contact with fresh ion-exchange resins will shift pH and may cause protein destabilization.**
- **Whey is first introduced into cation exchanger, where positively charged ions (Na<sup>+</sup>, Ca<sup>2+</sup> etc.) are replaced with H<sup>+</sup>.**
- **Whey is then pumped in an anion exchanger where all the negatively charged ions (Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, etc.) are replaced with OH<sup>-</sup>.**
- **Ion exchange of whey can be carried out at > 50°C, if it has previously been deproteinized.**
- **If whey is not deproteinized, protein destabilization and loss during ion exchange can be avoided by using 5-12°C.**

- Ion exchange is actually a batch process.
- Transfer of whey through resin beds continues, until resins are saturated with cations and anions.
- This point is controlled by means of conductivity meter, after which resin beds are purged of whey, washed with water and regenerated by means of acid and alkali solutions.
- These solutions should be sufficiently concentrated to remove absorbed cations and anions and replace them by  $H^+$  and  $OH^-$  bringing them back to their previous state.
- After regeneration, resins are washed with clean water, preferably condensate from an evaporator.
- After this, the process can start again.
- Production line consists of ion-exchange vessels, storage tanks for chemicals, feed and product storage, pumps, valves and dosing systems, water supply, and refrigeration system.
- With one-line configuration consisting of typical 2 h of production and 4 h of regeneration, four cycles can be performed per day, i.e., 8 h of productive work. Two parallel lines provide 16 h of production, and three parallel lines provide 24 h of production.



- After its passage through both exchanger columns, whey is demineralised, depending on its type, from 90-98%.
- Processing/holding time is 20 min.
- Processing temperature is <10 C.
- Whey that has been demineralised up to 90% can be directly concentrated and dried.
- Obtained powder is non-hygroscopic.



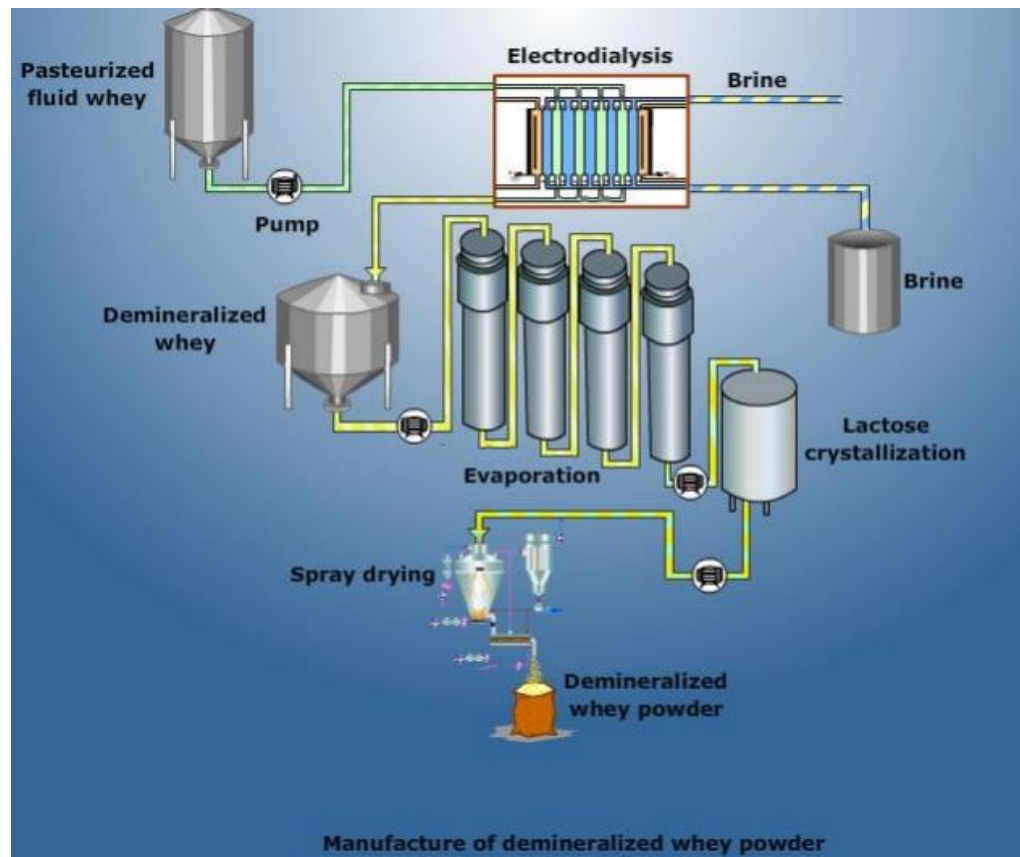
- **After completion of operation or on exhaustion of resin, residual whey is flushed out.**
- **Flushing normally uses 2 bed volumes.**
- **Back washing may be employed, which results in expansion of bed as a result of reverse flow and allows easier removal of physically entrapped material.**
- **After washing, resins are regenerated through introduction of regenerate solutions (generally 3 to 10 bed volumes for cation exchangers and 3 to 5 bed volumes for anion exchangers).**
- **Regenerant solution is then finally resumed.**
- **Deionized water used for final rinse is derived from the condensation water supply of evaporator (up to 10 bed volume).**
- **Na<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>OH are used as regeneration solution for anion exchangers.**
- **Sanitization is possible after regeneration stage using sodium isocyanurate solution.**
- **Counter current re-generation minimizes amount of regenerating agent.**

## SMR Process

- In SMR process, whey first enters anion column, where whey anions are exchanged for  $\text{HCO}_3^-$ -ions.
- After this, whey enters cation column, where cations of whey are exchanged for  $\text{NH}_4^+$  ions.
- After the process, whey salts are thus exchanged for ammonium bicarbonate.
- Ammonium bicarbonate is thermolytic salt which decomposes to recoverable  $\text{NH}_3$ ,  $\text{CO}_2$  and water, when heated during subsequent evaporation of whey.
- Plant using SMR system at Arjang, Sweden, has achieved 70% recovery of  $\text{NH}_3$  and 90% recovery of  $\text{CO}_2$ , with plant yield of 85%.
- Of 15% yield loss of more than two thirds is due to demineralization.
- Other losses are <5% and protein losses were <1%.

# Electrodialysis vs. Ion Exchange Process

- Electrodialysis is very capital intensive, whereas ion exchange has high operating cost.
- Cost for electrodialysis demineralization is greatly dependant on conductivity and, therefore, increases with reduced ash content.
- Consumption of 10-28 KWH of electrical energy must be considered for each kg of demineralised whey powder.



## Composition of two different demineralised whey powders

Composition	Whey Powder	
	50% Demineralised	90% Demineralised
Fat	0.6 - 0.9%	0.6 - 0.9%
Protein	12.0 - 14.5%	13.0 - 15.5%
Lactose	75 - 80%	80 - 85%
Mineral Salts	4.0 - 5.0%	0.7 - 1.0%
Sodium	0.4 - 0.5%	0.06 - 0.12%
Potassium	0.6 - 1.0%	0.25 - 0.3%
Chloride	0.1%	0.05%
Calcium	0.6%	0.15%
Phosphorus	0.4%	0.14%
pH in 5% Sol.	6.4 - 6.9	6.4 - 6.9
Solubility Index	< 0.1 ml	< 0.1 ml
Total counts	< 3000/g	< 3000/g
Yeasts of Moulds	< 10/g	< 10/g
<i>B. cereus</i>	< 200/g	< 200/g
Faecal streptococci	< 100/g	< 100/g
Coagulose +ve staphylococci	Nil in 1 g	Nil in 1 g
<i>E. Coli</i>	Nil in 10 g	Nil in 10g
<i>Coli aerogenes</i>	Nil in 0.1 g	Nil 0.1g
<i>Salmonella, shigella</i>	Nil in 50 g	Nil in 50 g

## **Nanofiltration (Loose Reverse Osmosis)**

- **Electrodialysis and ion-exchange processes are effective, but are limited by high capital cost, high running cost and high level of effluents.**
- **Ion exchange is relatively non selective and removes both monovalent and polyvalent ions, whereas; electrodialysis is more dependent on ionic mobility and tends preferentially to remove monovalent ions.**
- **Nanofiltration is a membrane separation process which allows selective passage of water, salts and very low molecular wt organic molecules.**
- **Membrane pore size used is 10-50 Å and operating pressure used is about 300 psi.**
- **Today, there are many plants utilizing this technology for partial demineralization of sweet whey, hydrochloric acid casein whey and ultrafiltration permeates.**
- **Advantage: Water is also removed from product during operation, and significant degree of concentration (>20% solids) is also achieved.**