The Indian Council of Agricultural Research has established a Centre of Advanced Studies in Dairy Technology with the objective of strengthening the on-going teaching and research programmes in Dairy Technology at the Institute. The mandate of the Centre is also to improve the competence of teachers in State Agricultural Universities and Dairy Science Colleges in India through regular interactions.

The world in recent times has witnessed many significant developments in Food Science and Technology in general and Dairy Technology in particular. It is heartening to note that many of the Dairy Technology Scientists working at the Institute have received advanced training and research experiences in countries like Germany, USA and Australia in the different membrane systems as applied to processing of milk and milk products. The Membrane Technologies encompassing reverse osmosis, ultrafiltration, nanofiltration and microfiltration have found diverse application in the dairy industry abroad. A beginning has already been made at this Institute to exploit these technologies for pilot scale production of certain novelty and value-added products. Indian dairy industry is expected to adopt many of these technologies in the near future.

It is appropriate that a short training course in Recent Advances in Membrane Technology is being organized by the Dairy Technology faculty at this Institute. It is hoped that the present compilation of information in the form of lecture notes by the various scientists of the Institute and guest speakers will be of great relevance to the participants in their teaching and R&D endeavours. The R&D staff in the dairy industry will get equally benefited by these lecture notes. I wish to compliment the Dairy Technology faculty for their commendable effort in bringing out this document in a relatively short time.

18th March, 1996

( O. S. TOMER )
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ORGANIZING COMMITTEE

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Dr. S. Singh, Member
Dr. G. S. Rajorhia, Member
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Dr. A. A. Patel, Member
Dr. R. S. Mann, Member
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Dr. R. S. Patel, Course Coordinator

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Mr. F. C. Garg, Member
# RECENT ADVANCES IN MEMBRANE TECHNOLOGY

at

CENTRE OF ADVANCED STUDIES IN DAIRY TECHNOLOGY
DAIRY TECHNOLOGY DIVISION, NDRI, KARNAL

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<td>10.00 AM - 11.30 AM</td>
<td>Inaugural Function</td>
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<td></td>
<td>11.30 AM - 12.00 Noon</td>
<td>Tea</td>
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<td>12.00 Noon - 1.00 PM</td>
<td>Orientation and Visit of the Institute</td>
<td>Sh. D. K. Sharma</td>
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<tr>
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<td>2.30 PM - 3.30 PM</td>
<td>Overview of Membrane Technology in Relation to Industrial Applications</td>
<td>Dr. B. N. Mathur</td>
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<td>3.30 PM - 3.45 PM</td>
<td>Tea and Discussion</td>
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<td>3.45 PM - 4.45 PM</td>
<td>Visit to Computer Centre</td>
<td>Dr. D. K. Jain</td>
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<td>Principles, Classification and Characteristics of Filtration Process</td>
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<td>11.00 AM - 11.15 AM</td>
<td>Tea and Discussion</td>
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<td>11.15 AM - 12.15 PM</td>
<td>Principles and Characteristics of RO Process.</td>
<td>Dr. Dharam Pal</td>
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<td>12.15 PM - 12.30 PM</td>
<td>Discussion</td>
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<td>12.30 PM - 1.00 PM</td>
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<td>1.00 PM - 2.30 PM</td>
<td>Lunch</td>
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<td></td>
<td>2.30 PM - 3.30 PM</td>
<td>RO Membranes and Process Conditions for Practical Application</td>
<td>Dr. Dharam Pal</td>
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<td></td>
<td>3.30 PM - 3.45 PM</td>
<td>Tea and Discussion</td>
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<td>3.45 PM - 4.45 PM</td>
<td>Inorganic UF/MF Membranes</td>
<td>Mr. D. K. Sharma</td>
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<td>Hardware for Membrane Plant</td>
<td>Dr. R. S. Patel</td>
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<tr>
<td>11.00 AM - 11.15 AM</td>
<td>Tea and Discussion</td>
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<tr>
<td>11.15 AM - 12.15 PM</td>
<td>Application of Nanofiltration in Dairy Industry</td>
<td>Dr. A. A. Patel</td>
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<tr>
<td>12.15 PM - 12.30 PM</td>
<td>Discussion</td>
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<tr>
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<tr>
<td>2.30 PM - 3.30 PM</td>
<td>Electrodialysis Process and its Application</td>
<td>Dr. V. K. Gupta</td>
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<td>3.30 PM - 3.45 PM</td>
<td>Tea and Discussion</td>
<td>Mr. Nilesh Badani</td>
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<td>3.45 PM - 4.45 PM</td>
<td>Guest Lecture</td>
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**MARCH 23, 1996**

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<tr>
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<td>Membrane Fouling Problems and Treatments</td>
<td>Dr. R. S. Patel</td>
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<td>11.00 AM - 11.15 AM</td>
<td>Tea and Discussion</td>
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<td>11.15 AM - 12.15 PM</td>
<td>Technology of UF-Channa</td>
<td>Mr. D. K. Sharma</td>
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<td>2.30 PM - 3.30 PM</td>
<td>Application of Ultrafiltration in Biotechnology</td>
<td>Dr. G. P. Agarwal</td>
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<td>3.30 PM - 3.45 PM</td>
<td>Tea and Discussion</td>
<td>(IIT, Delhi)</td>
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<td>Estimation of Membrane Parameters and Mass Transfer Coefficient in a Membrane</td>
<td>Dr. Sharad K. Gupta (IIT, Delhi)</td>
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*Sunday*

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<td>Application of UF/RO in Fruits and Vegetables</td>
<td>Mr. D. K. Sharma</td>
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<td>11.00 AM - 11.15 AM</td>
<td>Tea and Discussion</td>
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<td>Time</td>
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<td>Manufacture of WPC using UF Process (Practical)</td>
<td>Dr. V. K. Gupta and Mr. R. B. Puranik</td>
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<td>Manufacture of WPC using UF Process (Practical continued)</td>
<td>Dr. V. K. Gupta and Mr. R. B. Puranik</td>
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<td>Manufacture of WPC using UF Process (Practical continued)</td>
<td>Dr. V. K. Gupta, Dr. R. S. Mann and Mr. R. B. Puranik</td>
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<td>1.00 PM - 2.30 PM</td>
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<td>Manufacture of WPC using UF-Process</td>
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<td>3.30 PM - 3.45 PM</td>
<td>Tea and Discussion</td>
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<td>3.45 PM - 4.45 PM</td>
<td>Mechanization of Paneer</td>
<td>Dr. K. V. S. S. Rao</td>
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<td>10.00 AM - 11.00 AM</td>
<td>Ultrafiltration Technique for Shrikhand Manufacture</td>
<td>Mr. D. K. Sharma</td>
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<td>11.00 AM - 11.15 AM</td>
<td>Tea and Discussion</td>
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<td>11.15 AM - 12.15 PM</td>
<td>Manufacture of Low-Lactose Powder using UF-Technology</td>
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<td>12.15 PM - 12.30 PM</td>
<td>Discussion</td>
<td>Dr. R. S. Patel</td>
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<td>2.30 PM - 3.30 PM</td>
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<td>Dr. Dharam Pal</td>
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<td>Tea and Discussion</td>
<td>Dr. R. S. Patel</td>
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<td>3.45 PM - 4.45 PM</td>
<td>Manufacture of Whey Powder using RO</td>
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<tr>
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<td>Ultrafiltration of Milk (Practical)</td>
<td>Dr. R. S. Patel and Dr. R. S. Mann</td>
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<td>1.00 PM - 2.30 PM</td>
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<td>2.30 PM - 3.30 PM</td>
<td>Microfiltration and its Applications in Dairy Industry</td>
<td>Mr. D. K. Sharma</td>
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3.30 PM - 3.45 PM  Tea and Discussion
3.45 PM - 5.00 PM  Use of UF-Retentate for Paneer Making (Practical)  Dr. S. K. Kanawjia and Dr. R. S. Patel

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11.00 AM - 11.15 AM  Tea and Discussion
11.15 AM - 12.15 PM  Use of Reverse Osmosis in Kheer Making  Dr. G. S. Rajorhia
12.15 PM - 12.30 PM  Discussion
12.30 PM - 1.00 PM  Library Consultation
1.00 PM - 2.30 PM  Lunch
2.30 PM - 3.30 PM  Manufacture of Lactose using Membrane Technology  Dr. V. K. Gupta
3.30 PM - 3.45 PM  Tea and Discussion
3.45 PM - 4.45 PM  Application of UF in Cheese Making  Dr. S. K. Kanawjia
4.45 PM - 5.00 PM  Discussion

MARCH 30, 1996

9.30 AM - 1.00 PM  Concentration of Milk by RO (Practical)  Dr. Dharam Pal and Mr. D. K. Sharma
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2.30 PM - 5.00 PM  Rennet Coagulation Behaviour of UF Milk (Practical)  Dr. R. S. Patel and Mrs Latnha Sabikhi

MARCH 31, 1996

SUNDAY

APRIL 1, 1996

Holiday

APRIL 2, 1996

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11.15 AM - 1.00 PM  Indigenous Products from RO Concentrate (continued)  Dr. Dharam Pal and Mr. F. C. Garg
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**Lunch**  
Functional Properties of WPC  
Dr. V. K. Gupta  
Tea and Discussion  
Dr. A. A. Patel  
Heat Stability and Age Gelation of Membrane Concentrated Milks  
Discussion  

**APRIL 3, 1996**  
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Dr. B. N. Mathur  
11.00 AM - 11.15 AM  
Tea and Discussion  
Dr. V. K. Gupta  
11.15 AM - 12.15 PM  
Use of WPC in Dairy and Food Products  
Dr. V. K. Gupta  
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Discussion  
12.30 PM - 1.00 PM  
Library Consultation  
1.00 PM - 2.30 PM  
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**APRIL 4, 1996**  
10.00 AM - 12.00 Noon  
*VALEDICTORY FUNCTION*  
Director NDRI and Faculty Members
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<td>Principles, Classification and Characteristics of Filtration Process. Dr. R. S. Patel</td>
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<td>RO Membranes and Process Conditions for Practical Application. Dr. Dharam Patel</td>
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<td>Inorganic UF/MF Membranes. Mr. D. K. Sharma</td>
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<td>Hardware for Membrane Plant. Dr. R. S. Patel</td>
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<td>Application of Nanofiltration in Dairy Industry. Dr. A. A. Patel</td>
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<td>Membrane Fouling Problems and Treatments. Dr. R. S. Patel</td>
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<td>Manufacture of Low-Lactose Powder using UF-Technology. Dr. R. S. Patel</td>
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<td>Manufacture of Whey Powder using RO. Dr. R. S. Patel</td>
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<td>Microfiltration and its Applications in Dairy Industry. Mr. D. K. Sharma</td>
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<td>Use of Reverse Osmosis in Kheer Making. Dr. G. S. Rajorhia</td>
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<td>Use of WPC in Dairy and Food Products. Dr. V. K. Gupta</td>
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<td>Cleaning of UF/RO Membranes. Dr. R. S. Patel</td>
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OVER-VIEW OF MEMBRANE TECHNOLOGY AND ITS APPLICATIONS IN THE DAIRY INDUSTRY

Dr. B. N. Mathur,
Head, Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Since the industrial introduction of Reverse Osmosis and Ultrafiltration during 1960s, later R&D efforts in membrane technology have led to the development of additional pressure driven separation processes. Four membrane processes are now in vogue in the dairy industry namely, Reverse Osmosis, Ultrafiltration, Microfiltration and Nanofiltration. These processes are characterised by the particulate size related exclusion ranges of the membranes employed. These developments have opened up new vistas for product and process development that can have a profound effect on the dairy industry as a whole. However, there is paucity of information regarding technical information on membrane evaluation tests feed rates, cross flow velocities, cleaning procedures, nature of membrane fouling and economics of membrane replacement, which are all not always comprehensively reported in the published literature. Research or industrial trials are, therefore, of limited implications. For the introduction of membrane processing in the Indian Dairy Industry, there are additional constraints of high initial capital cost of the equipment, lack of indigenous back up support for replenishment of membranes, inadequate technological expertise of plant operators in terms of their capability for maintaining trouble free processing conditions.

This paper gives an over view of the various types of membranes being currently used in the dairy industry and the innovative applications that have been developed to evolve various processes and range of dairy products with unique functional characteristics.

2. RANGE OF MEMBRANE PROCESSES

i. Microfiltration (MF):

This pressure-driven membrane separation process uses porous membranes with cut-off pore sizes in the region of microns ($10^{-7}$ m), allowing passage of proteins but retains fat globules; microorganisms and somatic cells. In the literature, terms "cross flow" or tangential flow" microfiltration have been used to signify that the fluid flow is tangential to the membrane surface and perpendicular to the permeate flow through the membrane so as to counteract the formation of deposit layers. In this process, typical operative pressures are somewhat lower and fluxes about 1 order to magnitude higher than for the classical UF. The process may also be described as a "loose UF".

ii. Ultrafiltration (UF)

This process typically employs membranes with molecular cut-of in the range of 10000 - 75000 D. In the dairy industry, traditional application of UF is in the separation
and fractionation of individual milk proteins from lactose and minerals. Significantly, the permeate stream is 'sterile' due the retention of microorganisms. Other industrial applications include enzyme recovery in various operations, for example, lactose hydrolysis by soluble lactase preparations.

iii. Nanofiltration (NF):

The principal application of this membrane process is for separation of mineral ions in the $10^9$ m size exclusion range. The membranes that are available industrially serve the useful purpose of selective rejection of ions based on their charge. The main emerging applications for the dairy industry are in partial demineralization of whey. Effectiveness of NF is also in terms of the removal of mineral ions that contribute significantly to the osmotic pressure in process fluids. The operating pressures employed are generally lower than the pressures used by RO due to the larger pore size of the membranes, which is sufficient to retain most of the lactose. In this manner, the process could also be viewed as an ultratight UF as well as a loose RO. The theoretical basis for the mass transfer mechanism appears to be a mixture of diffusion and pore flow.

iv. Reverse Osmosis (RO)

Synonymous with the term "hypermembrane", this process permits concentration based on the removal of water molecules only. Most of the industrially available RO membranes may not always permit complete retention of all the solutes due to mechanical imperfections or molecular diffusivities comparable to that of water, thus over-lapping NF in a limited sense. The tight nature of the membranes calls for the highest operating pressures compared to the other membrane separation processes.

3. OPERATING PROBLEMS

Fouling of membranes represents major problems area and calls for special knowledge of operating skills and cleaning procedures. Current R&D emphasis is, therefore, focused on minimising fouling. The mechanisms of fouling are often dependent on the porosity of membranes and the physico-chemical properties of the membrane surface. Among the prominent foulants are native proteins and bacteria. Fat globules, denatured proteins and cell debris are involved in pore plugging. Other factors causing fouling are adsorption, concentration, polarisation and gel layer formation. Additionally electrostatic effects also reduce trans membrane flow rates. Temperature related influences include both native and denatured proteins as well as calcium phosphate. Manufacturers of membranes have been constantly involved in developing membranes to minimise fouling effect. Various approaches may be categorized as follows:

i. The high degree of control of pore size distribution in ceramic membranes.
ii. The decreasing rugosity of the ceramic filtration layer
iii. The development of systems based on pulse flow conditions.
iv. The control of hydrophilicity of the capillary membranes, which is often temperature dependent.
Additionally, modification of the engineering design features of membrane equipment such as increasing the product spacer, recirculation loops, flow distribution with more housings in parallel CIP arrangements also contribute significantly to control of fouling during membrane processing.

For minimizing fouling of membranes certain pre-treatments of the liquid feeds help to minimize fouling of membranes, viz:

i) Reduction of fines in the feed
ii) Reduction of free fat in butter milk whey and milk
iii) Partly denatured whey proteins reduce flux rate more prominently compared to total denatured proteins. pH in the range of 5.9 to 6.0 minimizing calcium phosphate fouling.
iv) pH in the range of 4.8-5.8 generally results in poor flux due to proteins.
v) Use of citric acid for pH adjustment minimizes fouling by binding calcium
vi) Free Air gives more fouling due to restriction of recirculation fluids.

4. NEW APPLICATIONS OF MEMBRANE PROCESSING

4.1 Milk Protein standardization:

A symposium "Milk Protein Standardization" organized by the International Dairy Federation during 1994 concluded "There appears to be no technological, consumer or nutritional reasons which would prevent protein standardization of milk and milk products". Standardization of protein content of milk and milk products has become an international issue and receiving attention of the planners and research workers alike. Views on protein standardization of fluid milk for drinking, other fluid milk products and cream are receiving considerable attention in context with the economic implications of protein standardization. Some of the issue involved are: What are the benefits / costs of protein standardization for drinking milk for the dairy industry and the consumer; What will happen if protein standardization of drinking milk is legalized and how is it to be achieved. Many countries are working on identifying the economic, legal and marketing issues regarding milk protein standardization and have proposed solutions; There is a need to inform the dairy industry and Government officials at the international level regarding issues and solutions; and , identify ways of informing the consumer about these issues. From processing point of view these issues can be attempted most effectively through the appropriate application of membrane filtration.

4.2 RO for Bulk Transportation of Raw Milk

There has been considerable interest in utilising the potential of RO for reducing the bulk of raw milk to economise the transportation costs. Extensive studies have been carried out on the techno-economic feasibility of the process. Various operating parameters have been standardised for the optimisation of the process.
4.3 Fractionation of Milk Proteins

Application of membrane processing based on particle or molecular size has opened up new possibilities for fractionation of milk proteins into various constituents having unique functional characteristics. Theoretically, most milk proteins should be separable directly by selective membrane filtration of skim milk. Form the largest size to the least as follows: lipoproteins in milk fat globule membrane > casein micelles > immunoglobulins > lactoferrin > serum albumin > β-lactoglobulin > α-lactalbumin > casein-derived peptides. Such work is in progress at CSIRO Division of Food Science & Technology Australia and New Zealand Dairy Research Institute, New Zealand. An exciting advance with commercial potential, is the combination of ion exchange properties in a membrane configuration. Such ion exchange membranes allow rapid recovery with high selectivity and appear specially suited to low yield applications such as preparation of lactoferrin, lactoperoxidase etc.

4.4 Demineralization and Delactosation of Dairy Products

Nanofiltration represents a major advancement in the area of membrane processing. However, it distinguishes itself from ultrafiltration in terms of allowing selective rejection of low molecular weight species and particularly the monovalent ions during the course of concentration. The extent of ash reduction by NF is primarily dependent on the pH of the whey. The degree of demineralization for rennet whey, cheese whey and acid casein whey provides more interesting challenges. Poor permeation of chloride following neutralization of acid whey calls for additional treatment of whey through addition of citrate. Non-protein nitrogen of less than 12000 D accounts for most of the nitrogen loss. Lactose rejection during NF ranges between 1000-2590 mg/litre over the course of 4x concentration. Whey can be demineralized and concentrated simultaneously to approximately 25 percent total solids and 47 percent demineralization. NF is a good alternative for the traditional method of concentration and demineralization of whey by evaporation and electrodialysis.

4.5 Processing of Evaporator Condensate

An Austrian Dairy requires 800000 litres of hygienic quality water for processing of milk and produces about 550,000 litres per day of condensate from evaporation of milk and whey. The condensate contains micro-organisms, trace fat and proteins as well as miscellaneous organic and inorganic compounds which is disposed as waste water following heat recovery. The Dairy has successfully developed combination of ultrafiltration / Reverse Osmosis processes which effectively removes impurities and helps to recycle water.

4.6 Preparation of Biological Peptides

Enzymic modification of milk proteins permits development of peptides having unique physico-functional properties having pharmacological significance. Many of the nutritional and therapeutic attributes of cheese and fermented milk products have been attributed to the physiological role of bio-peptides derives from milk proteins. These bio
peptides have been implicated in physiological roles such as biotransfer of trace elements, immunomodulation, antihypertension, antithrombosis, regulation of the gastrointestinal tract and the general behaviour (Morphine like activity). Membrane ultrafiltration is being used as the most appropriate tool for separating low molecular weight peptides and free amino-acids from proteins substrates utilizing enzymes. Considerable work is under progress at the Dairy Research Laboratory, INRA France, Universite Laval, Canada and Dept. of Pharmacology, University of Hamburg, Germany.

4.6 Production of Pasteurized Milk with extended Shelf Life

Micro-filtration process can be effectively employed for reducing the bacterial counts in skim milk by more than 99 %. Subsequently treatment of skimmed milk and its re-add mixture with cream permits production of superior quality of pasteurized milk with extended shelf life.

5. EPILOGUE

Rapid developments in the range and capabilities of membranes have the potential to profoundly effect the dairy industry as a whole. Being an excellent tool for the fractionation of milk proteins, a new range of products having unique nutritional and functional characteristics (gelling, foaming, emulsification, water holding capacity) have been developed by employing membrane processing. More recently, membrane processes have been utilised for the preparation of enzymatic derivatives of milk proteins having pharmacological significance. Reduction of bacteria by microfiltration permits a unique approach for the improvement of the quality parameters of dairy products such as flavour, and extended shelf life. Dairy industry in India is seriously handicapped at present due to the lack of infrastructural support for the supply of membrane modules, detergents for cleaning and sanitation as well as lack of engineering support for the maintenance of the range of equipments employed for membrane processing. Operation of membrane processing equipments requires special expertise which is essential for maintaining a trouble free operation of the manufacturing processes. It is important to develop suitable strategies to overcome these difficulties through strategic planning to pave way for the application of membrane processing in India.

6. SELECTED REFERENCES

## Spectrum of Application of Membrane Separation Processes

<table>
<thead>
<tr>
<th>Particle size ((\nu))</th>
<th>0.0001</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1.0</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW (D)</td>
<td>100</td>
<td>1000</td>
<td>10,000</td>
<td>100,000</td>
<td>500,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle</td>
<td>ionic</td>
<td>molecular</td>
<td>macromolecular</td>
<td>cells</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk System</td>
<td>ions</td>
<td>WP</td>
<td>fat</td>
<td>yeats</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>salts</td>
<td>caseins</td>
<td>bacteria</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>lactose</td>
<td>vitamins</td>
<td>protein aggregs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>RO</td>
<td>UF</td>
<td>NF</td>
<td>MF</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. INTRODUCTION

Filtration processes are usually classified according to the molecular size of components retained by the filter media. However, two major classes can be identified: conventional particle filtration and membrane filtration. Conventional particle filtration is usually used in the separation of suspended particles larger than 10 microns while membrane filtration separates substances of molecular size less than 10 microns (Renner and El Salam, 1991). In addition, several differences can be recorded between these two filtration processes:

(i) The filter media used: A thick open structure is usually used in conventional particle filtration while in membrane filtration a thin membrane of control pore size is used.

(ii) Pressure used: In membrane filtration the use of the pressure is essential as the driving force for separation, while in particle filtration the pressure is applied only to accelerate the process. Gravity is the main force effecting particle separation.

(iii) Process design: The design of the membrane filtration is basically different from the conventional particle filtration. The flow of the feed stream in conventional filtration is perpendicular to the filter media and filtration can be conducted in an open system. In membrane filtration a cross flow or tangential flow design is followed.

(iv) Degree of separation: In conventional particle separation, suspended material can be separated completely from the liquid, while membrane filtration can only concentrate the retained materials in smaller quantities relative to the original liquid.

2. THE MAJOR MEMBRANE PROCESSES

2.1. Ultrafiltration (UF)

Ultrafiltration can be defined as a pressure driven membrane process that can be used in the fractionation, purification and concentration of the substances, having a molecular weight between $10^3$ to $10^6$ daltons. It consists merely in pumping the feed solution under pressure over the surface of a suitable supported membrane of the appropriate chemical nature and in the optimum physical configuration. In the UF process, the pressure gradient across the membrane would force the solvent and smaller species through the pores of the membrane, while the larger molecules would be retained. The retained phase "retentate" or concentrate as it is referred to, will thus be enriched in the retained macromolecules, while the permeate stream will be depleted of the macromolecules. The retentate will of course contain some of the permeate solutes also (Cheryan, 1986; Renner and El-Salam, 1991).
2.2. Reverse osmosis

In a normal osmosis solvent passes from the solvent side of the membrane through to the concentrate side thus diluting the solution and at the same time setting up a pressure. If an external pressure greater than the osmotic pressure is applied on the concentrate side, the process may be reversed, and solvent will be pushed out of the concentrate back in to the solvent side. This is the principle of RO. On this principle has been built a technology for concentrating solutions or for purifying solvents by controlling either the concentrate or the filtrate according to the product required (Glover, 1985). Reverse osmosis can be used for either purification or concentration. Production of pure water is an example of purification in which the contaminated water passes over the membrane and the pure water is recovered as permeate. For concentration, the components retained by the membrane constitute the product and permeate, usually water, is discarded. Concentration is the more difficult process, since it intensifies all the problems of concentration polarization by the nature of the process. It is well known that both UF and RO constitute the first continuous molecular separation processes that do not involve a phase change or inter phase mass transfer.

3. ADVANTAGES AND LIMITATIONS OF THE UF AND RO PROCESSES

Looking to the fact that the UF and RO have gained world-wide acceptance, it is of utmost importance to have a glance over the in-built advantages, which these processes offer (Glover, 1985; and Patel et al., 1987).

(i) RO and UF are perhaps the first continuous molecular separation processes that do not involve either a phase change or interphase mass transfer.

(ii) Energy requirements of membranes processes are very low compared with other processes such as evaporation, freeze concentration, and freeze drying.

(iii) Membrane processes can be operated at ambient temperature, thus, thermal oxidation degradation problems common to evaporation processes, can be avoided resulting in better nutritional and functional properties of milk constituents.

(iv) There are minimum changes in the pH, and ionic strength of the feed being used.

To replace an old system with the new one generally only its advantages are considered, but for a balanced approach, the inherent limitations of the new process being adopted must also be taken in to consideration. Membrane processes are quite limited in their upper solids limits. Neither RO nor UF can take the solute to complete dryness in RO, it is frequently the osmotic pressure of the concentrated solute that limit the process, where as in UF it is high viscosity of the retentate that makes pumping of the retentate difficult and thus limit the process. The upper practical limit for concentration of buffalo skim milk and buffalo milk employing RO is 26 and 35% (Patel et al., 1992) total solids, respectively, and about 27 and 43% total solids using UF for buffalo skim milk and buffalo milk, respectively. Other problems such as the fouling and cleaning of membranes are some of the limitations of these technologies.
4. CHARACTERISTICS OF THE MAJOR MEMBRANE PROCESSES

Membrane filtration is subdivided into four classes according to the molecular size of the retained solutes. However, no sharp boundaries exist between these classes and usually there is an overlap between the molecular size that can be separated by these processes.

In addition to the ultrafiltration (UF) and reverse osmosis (RO) process, microfiltration (MF) and nanofiltration (NF) are also included as descriptive terms characterising specific new applications of the membrane separation technology. It may be argued that contrary to the conceptual differences between the UF and RO principles, MF and NF are not new distinct processes, but rather modifications of the RO and UF approaches based on specific membrane properties. However, from the standpoint of the dairy industry usage, it appears convenient to adopt these terms for characterisation of the specific membrane process applications. (See table 1):

4.1. Reverse Osmosis (RO)

(i) In this process only water passes through the membrane; everything else, including ions, organic molecules over a molecular weight of about 100 daltons remains in the concentrate (Marshall, 1985; Pepper and Pain, 1987).
(ii) Pore size is about 1 to 10 Å.
(iii) Operating pressure: 1500 Psig.

4.2. Ultrafiltration

(i) Ultrafiltration can achieve extremely clean separations of different size molecules e.g. The membrane allows the smaller molecules like lactose and salts to pass through while retaining large molecules like protein (Glover, 1985; Cheryan 1986; Eckner and Zottola, 1992).
(ii) Pore size of the membrane: 100Å to 1000Å.
(iii) Operating pressure: 10 to 200 Psig.

4.3. Microfiltration

(i) It is essentially a clarifying operation to remove suspended particles, including solids, milk fat globules, bacteria and colloidal particles (Merin and Dauphin, 1990)
(ii) Pore size ranges from 0.1 to 10 micron.
(iii) Operating pressure 1 to 25 Psig.

4.4. Nanofiltration

(i) It is used for removing salts from whey. It allows monovalent ions and some divalent ions to pass, but retains organic molecules. (Kelly et al., 1992; Gues and Zall, 1992).
(ii) Pore size from 10Å to 100Å.
(iii) Operating pressure: 300 Psig.
Table 1. Pressure driven membrane processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Alternative terminology</th>
<th>Membrane alternative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>Cross flow MF, tangential MF</td>
<td>Tortuous path, capillary-pore, organic membranes, inorganic membranes, alumina, ceramic</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>-</td>
<td>Synthetic polymers, (Polysulphone) inorganic zirconium, oxide, alumina</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Loose and leaky RO ultraosmosis, intermediate RO-UF, RO with solute fractionation</td>
<td>Thin-film composite, e.g. polyamide on microporous poly sulphone (NF-40, NF-70, HC-50, NTR)</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Hyper-Filtration</td>
<td>Single polymer RO, Asymmetric Thin film composite</td>
</tr>
</tbody>
</table>

4. GLOSSARY OF TERMS USED IN MEMBRANE TECHNOLOGY

Angstrom (Å): A° unit of length = 10⁻¹⁰ cm.

Anion: A negatively charged ion resulting from dissociation of salts, acids or bases in aqueous solution.

Anion permeable membrane: Membrane containing a fixed positive polar group which will permit passage of anions (e.g., bicarbonate, chloride, Sulfate) and reject cations (e.g., sodium, calcium, magnesium, etc.).

Asymmetric: Defines a particular type of ultrastructure of the membrane in the plane perpendicular to the membrane surface. Usually implies that the surface where the separation occurs is more dense than the rest of the membrane body. The "skim" layer is usually present in membranes made by the phase inversion process (Cheryan 1986).

Backflush: Reverse flow of permeate (or solvent) through the membrane.

Boundary Layer: The region near a solid surface where fluid motion is affected by the surface. The boundary layer is a major resistance to transport (e.g. of heat, mass or momentum. To improve transport the thickness of the boundary layer must be reduced.

Cation: A positively charged ion resulting from dissociation of molecules in solution.

Cation permeable membrane: Membrane containing fixed negative charges or polar group which will permit passage of cations (e.g., sodium, calcium, magnesium) and reject anions (e.g., bicarbonate, chloride, sulfate).

Compaction: In RO and UF, it refers to the compression of the membrane, or "shrinkage" of the pores, upon the application of pressure that leads to a decline in flux with time. This flux decline is not the same as that due to fouling.

Concentrate: That portion of the feed solution that is retained (on the high pressure side) of the membrane. As a result of ultrafiltration, the retained components are usually more concentrated than they were in the original feed solution. The terms "concentrate" and "retentate" are used interchangeably.
Concentration Polarization (CP): The build-up of solutes close to or on the membrane surface. Solute is brought to the membrane surface by convective transport; solutes larger than the nominal MWCO of the membrane are retained by the membrane, while solutes smaller than the pores will freely or partially permeate through the membrane. Solutes not passing through the membrane will accumulate on the membrane surface, causing either an increased resistance to solvent transport or an increase in local osmotic pressure (either of which may decrease flux) and possibly a change in the sieving characteristics of the membrane.

Demineralization: Any process that removes minerals/salts from water, most commonly used with ion-exchange processes.

Desalination: The removal of inorganic salts, usually sodium chloride, from water. Most commonly used with purification of sea water or brackish water.

Diafiltration: The convective elimination of permeable solutes by the addition of fresh solvent (or other solution) to the retentate. Two modes of operation may be used in diafiltration viz. continuous and discontinuous.

Flow rate (Q): The volumetric rate of flow of fluid parallel to the membrane surface. This expressed in terms of volume/time (e.g., liters/min or gallons/minute). Flow rate is velocity (V) x cross-sectional area of the feed channel. Also sometimes termed "recycling rate" or "recirculation rate".

Flux (J): Amount of fluid passing through the membrane, i.e., the volumetric rate of flow of the permeate through the membrane. It is usually given of volume per unit membrane area per unit time, e.g., litres/m²/hour GSFD (gallons/ft²/day).

Fouling: Phenomenon in which the membrane absorbs or interacts in some manner with solutes in the feed stream, resulting in a decrease in membrane performance (lowering if the flux and/or increase in rejection of solutes). This is usually an irreversible and time dependent phenomenon, which distinguishes it from concentration polarization. While concentration polarization effects are affected by operating parameters such as velocity, pressure, temperature and feed concentration and should not be a function of time of operation fouling is primarily time-dependent and also partially concentration-dependent. Fouling effects can usually only be offset by shutting down the system and cleaning the membrane by chemical means.

Membrane Constant or Membrane Permeability Constant: Defined analogous to the heat transfer coefficient, as the ratio of the flux to the driving force. Expressed as litres/sq.m/hr/kPa, litres/sq.m/hr/atm or GSFD/psi.

Module: The membrane and its housing.

Morphology: Relates to the physical form or microstructure.

Permeate: That portion of the feed solution that passes through the membrane.

Volume Concentration Ratio (VCR): The ratio of the initial feed volume to the volume of retentate remaining at any time during ultrafiltration.

Weight Concentration Ratio (WCR): The ratio of the initial weight of feed solution to the weight of retentate remaining at any time during processing.

5. REFERENCES


PRINCIPLE AND CHARACTERISTICS OF REVERSE OSMOSIS PROCESS

Dr. Dharam Pal
Dairy Technology Division, NDRI (ICAR), Karnal-132 001

1. INTRODUCTION

The name "reverse osmosis" (RO) is derived from osmosis, the natural phenomenon which provides water to tree leaves and water to animal cells to support life.

Normal osmosis takes place when water passes from a less concentrated solution to a more concentrated solution through a semipermeable membrane (Fig. 1). A certain amount of potential energy exists between the two solutions on each side of the semipermeable membrane. Water will flow because of this energy difference from the less concentrated to the more concentrated solution until the system is in equilibrium. The addition of pressure energy to the concentrated solution will stop the transport of water across the membrane when the applied pressure equals the apparent osmotic pressure between the two solutions. The apparent osmotic pressure is a measurement of the potential energy difference between the two solutions.

![OSMOSIS Diagram](image)

**OSMOSIS**

Fig. 1.

As more pressure is applied to the more concentrated solution as shown in figure 2, the water will begin to flow from the concentrated solution to the less concentrated solution. The rate of water transport is a function of pressure applied to the concentrated solution, the apparent osmotic pressure (i.e., the difference in the absolute osmotic pressure of each solution, and the area of membrane being pressurized). The absolute osmotic pressure is the potential energy difference between any solution and pure water.
The RO and other processes are based on the semipermeable membranes of the appropriate physical and chemical nature to discriminate between molecules primarily on the basis of size, and to a lesser extent, on shape and chemical composition. The main role of a membrane is to act as a relative barrier. It should permit passage of certain components, called as permeate, but retain certain other components, called as retentate, of a fluid mixture. By implication, either the permeate or the retentate should be enriched in one or more components. The nature of membrane itself controls which component permeates and which is retained. The separation characteristics of different membrane process are shown in Fig.3 and Table 1.
Table 1: Characteristics of Principle Membrane Separation Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>MWCD (daltons)</th>
<th>Operational Pressure (psi)</th>
<th>Membrane Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse Osmosis</td>
<td>200-800</td>
<td>5-20</td>
<td>~50</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Most organics over 500</td>
<td>10-50</td>
<td>~50</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Most organics over 25-200</td>
<td>10-100</td>
<td>~60</td>
</tr>
<tr>
<td>Microfiltration</td>
<td>Large suspended 1-25 particles, some emulsion</td>
<td>2.0 μm</td>
<td>~70</td>
</tr>
<tr>
<td></td>
<td>most bacteria</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In its broader sense RO is essentially a dewatering technique. Nanofiltration a demineralizing process, Ultrafiltration a method for simultaneously purifying, concentrating and fractionating macromolecules or fine colloidal suspensions, and Microfiltration is a clarification process that separates molecules and particles on the basis of size and solubility (Cheryan, 1989). Generally particles in the order of more than 0.05 μm are retained by MF membranes in all the membrane processes, a significant pressure is required to drive liquid through the membrane. The pressure required, however, depends upon the size of the pores. RO membranes have the smallest pores while MF membranes have the largest pores and hence require the least pressure.

2. Separation mechanism of RO membranes

The key to effective separation using RO is the structure of the membrane. The active layer of modern RO membranes is believed to be very thin, approximately 5-30 nm, with a pore size of about 5-20 Å. This "skin" is on top of a more porous support layer. These "asymmetric membranes are supported on a porous backing, for example, fiberglass, filter paper, metals (SS), ceramics, sintered glass, etc. and assembled in a suitable physical configuration.

The actual basis of separation is still not completely understood. The "preferential Sorption-capillary flow" mechanism of Sourirajan (Sourirajan and Matsuura, 1985) is the most logical and probable. It is based on the Gibbs adsorption isotherm model.

Gibbs Adsorption Isotherm

\[
S = \frac{\gamma_2}{RT}(\frac{\delta \gamma_1}{\delta \gamma_2})_\sigma
\]

\[S = \text{Excess Solute}\]
\( C_2 = \text{Concentration of Solute} \)
\( \gamma = \text{Surface Tension} \)
\( \sigma = \text{Surface area} \)

In this model solutions containing salts whose surface tension increases with concentration, such as inorganic salts, will have a "nagative excess" of the solute adsorbed on the membrane surface i.e. there will be a layer of water molecules on the membrane surface. If the membrane contains pores of the appropriate size (twice the thickness of the water layer) and a pressure sufficient to overcome the osmotic pressure or chemical potential difference is applied, the adsorbed solvent (water) layer will flow through these pores (Fig. 4). Thus the control of the pore size and providing an appropriate membrane surface is critical to the success of RO.

![Diagram](image)

*Figure 4*. Schematic of preferential sorption-capillary flow mechanism for reverse-osmosis separations of sodium chloride from aqueous solutions

3. ADVANTAGES OF RO PROCESS

i) RO is a simple process. It consists merely of pumping the feed solution under pressure over the surface of a suitably supported membrane. The removal of water is accomplished without a change in phase or state of the solvent.

ii) The energy requirements of RO are very low compared with other water removal processes, like, evaporation, freeze concentration, freeze drying, etc. Table 2 compares the energy requirements of some common dewatering technique with RO.
Table-2: Energy requirements of some dewatering processes (Marshall, 1985)

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy requirements K Wh/1000/kg water</th>
<th>Complexity</th>
<th>Maintenance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation (open pan)</td>
<td>626</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Freezing</td>
<td>92</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Evaporators</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 or 4 effect</td>
<td>126-180</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5 or 7 effect of MVR</td>
<td>37-52</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RO desalination</td>
<td>4</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>RO milk</td>
<td>9-19</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

1 = least, 4 = most

iii) The processes can be operated at ambient temperature. Thus thermal or oxidative degradation problems, common to evaporation processes can be avoided. Thus the nutritional and functional properties of milk constituents, like vitamins, proteins, etc. are least affected. There may, however, be occasions when operation at considerably low temperature is necessary (for example, to prevent microbial growth problems or denaturation of heat sensitive compounds) or at higher temperature (for example, to minimize microbial growth problems or to lower the viscosity of retentate, thus lowering the pumping costs and improving mass transfer).

iv) No complicated heat transfer or heat generating equipment is needed, and the membrane operation which require only electrical energy to drive the pump motor, can be situated far from the prime power generating plant. Also no additional steam capacity need to be installed to handle the RO and UF Unit. Since no condensers needed, problems like thermal pollution and over loading or sewage treatment systems are avoided.

4. LIMITATIONS

- The RO process is quite limited in its upper solids limits. As an example, current technology permit skim milk to be concentrated by multi effect evaporation to about 50% total solids, while the upper limit using RO is about 25% total solids. It is the osmotic pressure that limit the concentration level in the RO process. The osmotic pressure of selected solutions/foods is given in Table 3.
Table 3: Osmotic pressure at 30°C

<table>
<thead>
<tr>
<th></th>
<th>——(PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (2%)</td>
<td>58.5M_w</td>
</tr>
<tr>
<td>Lactose (1%)</td>
<td>342M_w</td>
</tr>
<tr>
<td>B-lactoglobulin (1%)</td>
<td>18,000M_w</td>
</tr>
<tr>
<td>Milk</td>
<td>12% TS</td>
</tr>
<tr>
<td>Whey</td>
<td>6% TS</td>
</tr>
<tr>
<td>Orange Juice</td>
<td>12% TS</td>
</tr>
<tr>
<td>Sea Water</td>
<td>3.5% TS</td>
</tr>
<tr>
<td>Coffee extract</td>
<td>28% TS</td>
</tr>
</tbody>
</table>

- Other problems that plagued early membrane applications were the fouling of membranes, poor cleanability of some early modules, and restricted operating conditions, although some of these problems have been overcome through the development of superior membrane materials and improved module design.

6. REFERENCES

RO MEMBRANES AND PROCESS CONDITIONS FOR PRACTICAL APPLICATIONS

Dr. Dharam Pal
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Membrane is considered to be the heart of a membrane process because it acts as a selective barrier. It permits passage of certain components, water in case of RO, but retains other components. Selection of an appropriate material for the manufacture of membrane is, therefore, very essential. The ideal membrane for RO application would consist of an ultra thin imperfection free film of a polymeric material. The transport properties of the material should be such that water can pass through with little hindrance, while presenting a virtually impermeable barrier to all organic solids and salts. To provide a large flow rate of water (flux) a real polymeric material method must meet the following requirements:

- The material must possess hydrophillic groups.
- Ions and non-hydrogen bonding substances must not enter the membranes
- The material must be good film maker
- It must have high swelling characteristics
- The membrane should have high wet strength
- It must exist in extremely thin layer so that it offers least resistance to passage of water.

In addition to these basic requirements, the rejection or retention coefficients and compatibility of membrane towards temperature and pH are also important considerations. Modern RO membranes have retention coefficient, that is the fraction of any particular dissolved substance the membrane retain, of 0.999 to sugars and large molecules, 0.90 - 0.98 for smaller ions such as sodium and between 0 and 0.90 for various low molecular weight organic compounds.

2. MATERIALS FOR RO MEMBRANES

Over 130 materials have been tried for membranes, but all of these are not available for commercial use. Table 1 shows the different commercially available membranes for specific applications.

All these materials are not suitable for food applications. The most common materials used for manufacture of commercial RO plants for food applications are discussed here.
### Table 1: Commercially available membranes

<table>
<thead>
<tr>
<th>Material</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>MF, UF, NF, RO</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>MF, UF, NF, RO</td>
</tr>
<tr>
<td>Polysulphone</td>
<td>MF, UF</td>
</tr>
<tr>
<td>CA/TCA blend</td>
<td>RO</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>MF</td>
</tr>
<tr>
<td>Polyvinylidene fluoride</td>
<td>MF, UF</td>
</tr>
<tr>
<td>Regenerated cellulose</td>
<td>MF, UF</td>
</tr>
<tr>
<td>Polycrylonitrile</td>
<td>UF</td>
</tr>
<tr>
<td>Polyamide</td>
<td>UF, NF, RO</td>
</tr>
<tr>
<td>Polycarbonate track etching</td>
<td>MF</td>
</tr>
<tr>
<td>Polybenzimidazola</td>
<td>RO</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>MF</td>
</tr>
<tr>
<td>Polyvinylchloride (PVC)</td>
<td>MF</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA)</td>
<td>NF</td>
</tr>
<tr>
<td>Sulfonated polysulfone</td>
<td>NF</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II. Inorganic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>MF, UF</td>
</tr>
<tr>
<td>Zirconia</td>
<td>MF</td>
</tr>
<tr>
<td>Carbon Composite</td>
<td>UF/MF</td>
</tr>
<tr>
<td>Silica</td>
<td>MF</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>MF</td>
</tr>
</tbody>
</table>

#### 2.1 Cellulosic acetate and its derivatives (CA, DCA, TCA and their blend)

These are widely used, despite its limitations. All the major US-based RO companies continue to make CA membranes, in addition to the newer materials. These first generation membranes are asymmetric, generally manufactured by the Sourirajan method, with a thin dense layer on its surface (The skin usually 0.1-0.5 μ thick) formed on the top of a more open structure.

**Advantage of CA membranes are:**

- These appear to give very good combination of flux and rejection properties
- Easy to manufacture in a variety of configurations and pore sizes
- The raw material, cellulose, is a renewable material
- CA is comparatively more hydrophilic than other polymers

**Disadvantages of CA are:**

- Narrow temperature range, maximum recommended is usually 30°C
• Recommended pH range 4-6. Life of CA membrane is 4 yrs at pH 4-5, 2 yrs at pH 6 and few days at pH 1 or 9
• Poor chlorine resistance. Shock doses of 50 ppm are permitted but continuous exposure should be less than 1 ppm
• Highly biodegradable and susceptible to microbial attack
• CA undergo "creep" or "compaction" phenomenon to greater extent

2.2 Polyamide membranes (PA)

The first generation polyamide membranes were introduced by the Du Pont Company in 1968 in hollow fine fibres configuration.

The Advantages of PA are:

• PA membranes are capable of operating at higher pH range (4-11) and higher temperature (upto 60°C).

Disadvantages of PA are:

• The concentrated polymer solution is extruded in a spinnaret at higher temperature (80-90°C) thereby reducing the voidage. This results into very low flux. PA is extremely sensitive to chlorine.

2.3 Composite membranes

These so-called second generation "membranes have gained rapid interest in the RO field. With the development of thin-film composite membranes the RO process is being widely used in food applications. These are also "skinned membranes" but the "skin" is added on the top of the microcrystals support back in a two-step process, contrary to the Sourirajan's one step method. TFC membranes generally contain a polyamide (or polyurea) separating ultraskin on a more porous poly-sulfone or polyethylene supporting layer. These membranes are reported to have superior properties to first generation CA and PA membranes in all respects.

• Membranes are available for RO / NF applications only

Advantages of TFC Membranes are:

• TFC has better stability towards wide pH range (3-11)
• It can withstand elevated temperature (60°C)
• Some of the manufacturers claim that their membrane can tolerate upto 75°C.
• Improved rejection of organic solutes
• Improved durability

Limitations are:

• Sensitive to chlorine solutions
3. Manufacturing methods for microporous membranes

Manufacture of a membrane is not just an easy process. It depends on the resin percentage in solution, the amount of solvent, the speed of casting the mix, temperature on the surface, etc. To develop a membrane with desired thickness pore size and porosity, All these parameters have to be controlled to develop a membrane with desired thickness, pore size porosity. The various processes used for manufacture of membranes are given in Table -2.

Table 2: Methods for manufacturing membranes

<table>
<thead>
<tr>
<th>Process</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Phase inversion by</td>
<td>Polymers</td>
</tr>
<tr>
<td>- Solvent evaporation</td>
<td>Cellulose acetate, polyamide</td>
</tr>
<tr>
<td>- temperature change</td>
<td>Polypropylene, polyamide</td>
</tr>
<tr>
<td>- Precipitant addition</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>II. Stretching sheets of partially crystalline polymers</td>
<td>Polymers (PTFE)</td>
</tr>
<tr>
<td>III. Irradiation and Track Etching</td>
<td>Polymers (Polycarbonate, poly</td>
</tr>
<tr>
<td>IV. Molding and sintering of fine grains powder</td>
<td>Ceramics, metaloxide, PTFE, polyethylene</td>
</tr>
<tr>
<td>V. Coating or interfacial reaction (TFC membrane)</td>
<td>Polyurea , polyamide, polysulf</td>
</tr>
</tbody>
</table>

Phase inversion processes and TFC process are presently employed for manufacture of RO membranes. During phase inversion process, a homogenous solution is converted into two continuous phases, one which is rich in the membrane material and forms the structure (e.g. polymer) and a second which is rich in the pore forming material (e.g. liquid solvent). Phase inversion refers to the polymer going from discontinuous phase solution to a continuous structure membrane. TFC membranes are usually made either by interfacial reaction of monomers to form a polymer in situ on the surface of the porous support or by coating of a film forming polymeric layer on top of porous support.

4. OPERATING PARAMETERS IN RO

The operating parameters that affect performance of membrane systems are:

- Pressure
- Feed Concentration
- Temperature
- Velocity / flow rate

4.1 Pressure: According to Hagen - Poiseuille Model,
flux for a particular membrane should be directly proportional to pressure of the feed solution and inversely proportion to viscosity:

\[ J = \frac{\varepsilon d^2 \Delta P}{32x \mu} \]

\( J = \) flow rate through pore (flux)
\( d = \) diameter of pore
\( \varepsilon = \) surface porosity
\( x = \) membrane "skin" thickness
\( \mu = \) viscosity of fluid
\( \Delta P = \) applied transmembrane pressure

Applied transmembrane pressure = \( \Delta P_T = \Delta \Pi \)
\( \Delta P_T = P_F - P_p \)
\( \Delta \Pi = \Pi_F - \Pi_p \)

\( \Delta P = \) hydraulic pressure
\( \Pi = \) Osmotic pressure
\( F = \) refers to feed
\( p = \) refers to permeate

The relationship between flux and transmembrane pressure is shown in Fig. 1.

The osmotic pressure and the membranes are the major flux limiting factors with RO. In UF and MF applications, the osmotic pressure of retained solutes are negligible and the major resistances to flux are the membrane, concentration polarization and associated boundary layer and fouling. Thus the direct relationship between applied
pressure and flux holds true only when a) the pressure is low b) at low feed concentration and c) at high feed velocities. Under all these conditions, the concentration polarization is negligible.

4.2 Concentration polarization

It occurs due to the convective movement of solids towards the membrane during processing. The rejected solids accumulate on the surface, causing a steep concentration gradient of solute within the boundary layer. This causes a back transport of retained solutes back to the bulk solution due to diffusion (Fig. 2.).

Eventually a steady state is reached where the two phenomena - the convective transport towards the membrane and the diffusive transport away from the membrane - balance each other. Soon the solute concentration in the concentration polarization layer reaches a maximum commonly known as the "gel concentration". It is due to this consolidated gel layer on the membrane that flux become independent of pressure. At this stage increasing the transmembrane pressure nearly results in a thicker layer. After a momentary rise, the flux will drop back to the previous value. Thus flux in the mass transfer controlled region will be controlled by the efficiency of minimizing boundary layer thickness and enhancing the rate of back transfer of polarized molecules.

4.3 Feed concentration

The flux will decrease exponentially with increasing feed concentration, as explained by film theory.

\[ J = K I n \quad \frac{C_G}{C_B} \]

where 
- \( J \) = flux
- \( C_G \) = concentration of solids on membrane surface
- \( C_B \) = feed concentration in bulk

According to this theory \( J = 0 \) when \( C_B = C_0 \).
Methods of increasing flux
4.4 Temperature

In general, higher temperature will lead to higher flux in both pressure-controlled and mass transfer-controlled regions. This assumes there are no other heat induced effects occurring simultaneously, such as salt precipitation, protein denaturation or other fouling phenomenon, that may confound the interpretation of the data. In the pressure-controlled regions, temperature favourably affects viscosity. The elevated temperature also increases the diffusivity. In general it is best to operate at the highest possible temperature consistent with limits of the feed and membrane.

4.5 Velocity (flow rate)

This is the velocity of the feed or retentate stream flowing tangentially or across the membrane. This turbulence, whether produced by stirring or pumping of the fluids has a major effect on fluxes in the mass transfer region. By increasing the velocity the accumulated solids near the membrane surface are swept away and the turbulence reduces the thickness of boundary layer.

Some of the methods for increasing flux have been depicted in the flow sheet (Fig. 3).

5. REFERENCES

INORGANIC UF/MF MEMBRANES

D. K. Sharma
Dairy Technology Division, NDRI (ICAR), Karnal 132 001

1. INTRODUCTION

A membrane is a barrier which is capable of redistributing components in a fluid stream through a driving force such as pressure difference, concentration or electrical potential. When a concentration or electrical potential gradient provides the necessary driving force, the separation process is called dialysis or electrodialysis, however most of the membrane processes (RO, UF and MF) are based on applied pressure difference across the membrane. Depending on the size of membrane pores the molecular sieving of components/constituents take place under the influence of the applied presence difference in the approx. range of 1 to 100 bars. Depending on the pore size on porous nature of membrane structure, the pressure driven processes are classified as Reverse Osmosis (RO), Ultrafiltration (UF) and microfiltration (MF).

Reverse Osmosis membrane are very dense or non-porous membranes, however, ultrafiltration and microfiltration membranes are conveniently defined as those having pore diameters in the ranges of 3-200 nm and 0.2-10 microns, respectively. Lonsdale (1982) has provided an excellent overview of membrane technology covering various developments and applications.

The barrier/membrane may be made of organic (polymers) or inorganic (mineral or ceramic) material. The first semi-permeable synthetic membrane was made-up of cellulose-Acetate. These membranes appear to give best combination of flux and rejection properties mainly in desalination of sea/brackish water. However these membranes are not suitable for food/dairy processing applications due to certain drawbacks such as limited operational ranges of pH (3-7) and temperature (35°C) and inability to withstand hypochlorite solution (50 ppm). These are highly bio-degradable and susceptible to microbial attack. Hence, normal sanitization with heat or chlorine to control sanitary environment of process is not possible with these membranes.

For application in dairy/food processes certain non-cellulosic membrane have been developed using a variety of synthetic materials such as nylon (polyamide), polysulphone, polyvinyl chloride, polystyrene etc. Some commercial polymeric membranes available in the market are given in Table 1 and Table 2.

Very recently materials like zirconium oxide, thorium chloride, aluminium oxide, carbon have been used to make porous membranes for wide range of applications in food and biotechnological processes. These porous membranes are called inorganic or mineral/ceramic membranes. In this article. We shall be discussing about these third generation inorganic membranes in detail.
2. HISTORICAL DEVELOPMENTS

Thomas Graham (1866) was the first person who observed that metallic palladium can absorb a large amount of hydrogen. Since his observation, palladium hydride system, has been studied extensively. Palladium based inorganic membrane systems and technology have been reviewed by Armor (1989) and Hsieh (1989). In addition to palladium and its alloys, other inorganic material have been found to be permeable only to certain gases. For example, silver and dense (stabilized) zirconium are only selective to oxygen. These palladium based non-porous membranes have not been used to any significant degree in conventional separation applications, probably due to their low flux and high costs.

In addition to palladium, several inorganic material have been investigated as precursors for porous membranes. Many of such materials are not commercialized yet. These include cordierite, mica, silica, silicon carbide, silicon nitride, tin oxide and titania.

Some other material intended for smaller pore size membranes have been prepared. Molecular sieve carbon membrane having pore diameter close to 0.5-1 nm have been made (Koresh and Sofer, 1983). Zeolite membranes have been attempted by reacting sodium silicate with caustic directly on the surface of porous sintered alumina to form sol followed by hydrothermal treatment.

Two membranes casting materials which had emerged for potential industrial application have been porous alumina and porous zirconia mainly for gas diffusion in uranium isotope enrichment for nuclear uses. The detailed quantitative information on the characteristic of these membrane is scarce due to security classification. The development of these gas diffusion membrane occurred independently to each other in United States in 1940's and in France in the 1950's.

Later in 1970's, Union Carbide refined the technology of Oak Ridge National Laboratories USA for commercialization of dynamic zirconia membrane and started marketing first commercial membrane under the brand name of Ucarsep® zirconia membrane for gas diffusion applications.

In France alumina membranes which were originally intended for gas diffusion had been further developed by Ceraver (now SCT, an Alcoa subsidiary) for commercial liquid filtration processes. Similarly, zirconia membranes developed in USA were further improved for liquid filtration processes by SFEC, France, with the technical backing of French Atomic Energy Commission. Now SFEC manufactures "Carbosep", the first mineral membranes commercially available.

Apart from France, only a small number of countries such as USA, Japan and more recently Holland, have tried to develop entirely mineral membrane for liquid separation. In India, there have been laboratory scale attempts to cast Alumina mineral membrane by the process of Anodic oxidation. These efforts are continuing with Atomic Research laboratories at Kalpakkam, Tamilnadu. Some of these commercially available porous inorganic membranes are tabulated as Table-3.
3. MINERAL MEMBRANE STRUCTURE

The mineral/ceramic membrane is composed of one or several layers of porous ceramic with well-defined texture. In case of several layers, the layers with the finest porosity forms the free surface of membrane and performs the separation. These layers are bonded in a monolithic way to each other and to the support by very strong ceramic bonds obtained by sintering operations.

The thickness of the separative membrane layer represents a balance between the physical integrity requirements on one hand and low flow resistance on the other. Current commercial show a membrane thickness as thin as approximately 5 μm, but generally in the 10-20 μm range. The bulk support needs to be in the range of few millimetres for mechanical strength. The intermediate layers range from 10 to 50 μm in thickness.

Commercially available 'Carbosep' membranes have sintered carbon as support material and layer of zirconia (zirconium oxide) as separating membrane. However, Ceraver has Aluminium oxide as both support material as well as separating layer. The typical characteristics of Carbosep membranes are given in Table-4.

4. MODULE

The membrane elements/modules are manufactured in different shapes such as tube, multi-channel monolith, disk or plate. In the carbosep modules tubular membranes are assembled in parallel bundles in stainless steel housing. The diffusing area of these modules range from 0.02 to 5.73 m² (see table-5) An other configuration may be multi-channel monolith as shown in Fig.-1. The modules provide the highest available filtration area per unit volume of a membrane element/module. Presently such modules are marketed under the brand name of 'Ceraver'. The characteristics of such modules which are commercially available is tabulated (Table-6).

In industrial applications, a membrane module might consist of more than a thousand tubes or many monoliths each of which contains 15 channels or more. It is obvious that the monoethic form makes installation and maintenance of membrane elements much easier.

Presently mineral/ceramic modules are not available in commonly available configuration such as 'hollow-fiber' and 'spiral-wound'. However, as the demand for inorganic membranes and the manufacturing technologies improve, in future, those high packing density elements may become a commercial reality.

5. INDUSTRIAL APPLICATIONS

Mineral/ceramic membranes has a wide range of applications in separation of gas and liquid phases in high temperature or corrosive environment of separation. Current commercial activities are mostly in the area of biotechnology including food processing (agri-foodstuffs) which demand high level of sanitation and clean
environment. This is the reflection of the instabilities of organic membranes (Polymeric) for industrially important processes involving high temperature and other corrosive environments.

Alumina membranes, currently available commercially, have pore diameter greater from 0.1 μm are found to be thermally, chemically and mechanically most stable and durable. Although these are stable up to about 1000°C, the modules are generally recommended below 140-150°C for those applications where steam sterilization is required. (Gillot and Garccra, 1984). This temperature limitations are due to the common sealing and potting material presently used in modules. It is possible to backflush these membranes with hot water for regenerating the initial flux during cleaning cycle. These membranes can be steam sterilized and also chemically cleaned with caustic soda followed by nitric acid and in the temperature range of 50-80°C, very similar to CIP cleaning of a food processing plant.

Alumina membrane have been used in variety of applications. Some of the typical application fields are:

i. Microfiltration of water for municipal supply; preparation of clean water for industrial uses, or treatment of reject water.
ii. Clarification and sterilization of beverages, wine, beer, fruit juice etc.
iii. Sterilization of liquids in the pharmaceutical industry.
iv. Cell harvesting and sterilization in biotechnological applications.
v. Ultrafiltration of milk and whey
vi. Filtration of viscous liquids including molten plastics.
viii. Filtration in chemical and nuclear industry.

These applications are very diverse and only few typical cases are discussed here:

- Ultrafiltration of whole or skimmed milk has been successfully performed on a microfiltration membrane with a pore diameter of 0.2μm (Bennasar, et al., 1989) with a protein recovery higher than 98%. Using velocity of 5 m/s and a pressure of 3 to 5 bars, an average flux of 80 litres/hr m² was obtained at 50°C when concentrating whole milk up to a factor of 5. Higher concentration can also be obtained if needed.

- Sharma et al., (1992) while studying the performance of ceraver ceramic microfiltration module (No. P-19-40) having 0.2 μm pore diameter at 50°C obtained excellent data on Ultrafiltration of different type of milks up to CF=4 which are tabulated as Table-7. Gouedranche et al., (1980) utilized mineral membrane for making semi-hard cheeses such as French variety St. Paulin. They claimed to reach a protein content of 21% and T.S. Content of 45% while Ultrafiltering milk using mineral membrane. Such high concentrations are not achievable by polymeric membrane yet. The average flux was 30 litres/hr m² for such high protein concentration. The membranes were easy to clean to regain initial flux.

- Microfiltration of wine has the same typical features as a number of filtration in food and beverage industry. With a pore diameter of 0.2 or 0.5 μm a very high limpidity
and sterility are obtained with fluxes that vary with the type of wine, but generally are of the order of 100 litres/h m². One of the major advantages of cross-flow microfiltration of wine is that it replaces in one single operation the many steps of the classical direct filtration process (Poirier, et al., 1984).

- Sharma and Reuter (1993, 1994) standardized processes for production of shirshand and charoma using mineral ultrafiltration modules and obtained 23% and 19% extra yields of product over traditional processes, respectively.

- In biotechnological applications, mineral membrane systems allow the coupling of a bioreactor or a biofermenter with ultrafiltration device. The UF-system forms an integral part of the fermenter when mineral membranes are used. This coupling offers the following main functions to the whole system:
  
  a. Joint sterilization of the fermenter and the UF-system.
  b. Continuous, controlled elimination by the UF of metabolites.
  c. Purification of biomass by continuous washing without exposure of air.
  d. Concentration of biomass under sterile conditions continuously.
  e. Sterile drainage and recovery.

On the whole, bioreaction and biofermentation yield are many fold boosted. Such coupled systems are operational for concentration of micro-organisms, the synthesis of amino acids and enzyme compounds, the extraction of biomolecules produced by fermentation, hydrolysis reaction of highly viscous complex media etc.

- The capacity to operate in totally sterile environment also endows these new membranes with potential applications, such as the preparation of thermally fragile biochemical solution by 'Cold' sterilization. The property is being utilized by the pharmaceutical industry.

6. TYPICAL CLEANING PROCEDURE FOR MINERAL MEMBRANES

6.1. Cleaning by backflushing

Backflushing is nothing but applying counter-pressure on filtrate or permeate side that pushes a controlled amount of filtrate back through the membrane thereby lifting the deposited matter on the membrane and indirectly cleaning the filtration area. The efficiency of this type of cleaning is dependant upon the type of suspension to be filtered and type of fouling that causes, but also upon the frequency and amplitude of the pulses of reverse pressure.

Short and frequent back pressure pulses, by constantly destroying this layer, maintain the filtrate flux at high value and enable a full exploitation of higher permeability of microfiltration membranes. This technique is one of the key advantages of ceramic/mineral membranes.

6.2. Cleaning by Chemicals
The membrane which are composed of alumina, a typical cleaning sequence that gives good results in dairy or wine filtration applications is as follows:

i. Water rinse: 10 min. at >15° C  
   (15 min. at ΔP=0.5 bar)  
   (5 min. at ΔP=1.0 bar)  
ii. Washing with 2 wt.% NaOH : 20 min.at 70°C  
   (15 min. at ΔP=0.5 bar)  
iii. Water rinse: 10 min. at > 15°C  
iv. Washing with 2 wt.% HNO₃: 20 min.at 70°C  
v. Water rinse: 10 min.at > 15°C  
vi. Sanitization with hot water at 95°C for min.or NaOCl solution with 100 to 200 ppm. free chlorine :10 min. at 20°C.

Depending on the type of fouling, using the same cleaning fluids in a different order may give better results.

Hence, the cleaning procedures is almost the same as adopted in CIP cleaning of food processing plant. The cleaning cycle does not demand special cleaning detergent or formulation as may be the case in polymeric membrane systems. It is easy and cheap to regain the initial flux in mineral membrane system after a well standardized cleaning cycle.

7. CONCLUSION

Historically the mineral membranes were developed in France and USA for "Gas diffusion" in Uranium isotope enrichment for nuclear uses. However, due to the greater, thermal, Chemical and mechanical stability of these membranes, these are used in wide variety of application now, mainly in biotechnological processes, food/dairy and chemical processes. Commercial ultrafiltration and microfiltration system are in operation mainly in France including EEC, USA, Russia, Japan etc. These systems are easy to clean by conventional CIP system and give higher flux and concentration because of its higher operational pressures and velocities. These systems are best in the processes which demand high level of sanitation and continuous operation especially in biotechnology, food processing and pharmaceutical processes. Coupling of minerals UF system with biofermenter are operational for concentration of micro-organisms, the synthesis of amino acids and enzyme compounds, the extraction of biomolecules produced by fermentation, hydrolysis reaction of highly viscous complex media. Still the mineral membrane system are costly and are only preferred where the end products are of very high value.

8. REFERENCES

Hsieh, H.P. (1988) ALCHE Symp. Ser. 84 (261), 1

Table 1 Ultrafiltration Membranes available to the Dairy Industry

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Dia or Chemical width (mm)</th>
<th>Composition</th>
<th>Cut off Min. Mol Wt.</th>
<th>Manufactured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tabular</td>
<td>25</td>
<td>Cellulose acetate</td>
<td>15,000</td>
<td>Abcor, USA</td>
</tr>
<tr>
<td>Tabular</td>
<td>24</td>
<td>CA &amp; Polyamide</td>
<td>10,000</td>
<td>Kalle, W. Germany</td>
</tr>
<tr>
<td>Tabular</td>
<td>17</td>
<td>-</td>
<td>7,000</td>
<td>Wafilin, England</td>
</tr>
<tr>
<td>Tabular</td>
<td>13</td>
<td>Cellulose derivative</td>
<td>22,000</td>
<td>PCI, England</td>
</tr>
<tr>
<td>Hollow Fibre</td>
<td>-</td>
<td>Modakry</td>
<td>50,000</td>
<td>Romicon, USA</td>
</tr>
<tr>
<td>Hollow Fibre</td>
<td>-</td>
<td>Polyamide</td>
<td>2,000</td>
<td>Kropp, W. Germany</td>
</tr>
<tr>
<td>Flat Plate</td>
<td>0.3-0.5</td>
<td>Polysulphone</td>
<td>20,000</td>
<td>DDS, Denmark</td>
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<tr>
<td>Flat Plate</td>
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<td>Non-CA</td>
<td>18,000</td>
<td>Dorroliver, USA</td>
</tr>
<tr>
<td>Flat Plate</td>
<td>2</td>
<td>Acrylic copolymer and poly sulphone</td>
<td>15,000</td>
<td>Rhone Poulenc, France</td>
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<tr>
<td>Flat Plate</td>
<td>2</td>
<td>-do-</td>
<td>50,000</td>
<td>Aqua Chem, USA</td>
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<tr>
<td>Spiral wound</td>
<td>0.8</td>
<td>Poly sulphone</td>
<td>1000</td>
<td>Osmonica, USA</td>
</tr>
<tr>
<td>Spiral wound</td>
<td>0.8</td>
<td>Cellulose acetate</td>
<td>600</td>
<td>Laidish, USA</td>
</tr>
</tbody>
</table>
Table 2: Reverse Osmosis Membranes available to the Industry

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Dia. or Channel Width (mm)</th>
<th>Salt Retention (%)</th>
<th>Water Flux (l/m²/hr)</th>
<th>Manufactured by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubular</td>
<td>25</td>
<td>90-98</td>
<td>38-19</td>
<td>Abcor, USA</td>
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<td>Tubular</td>
<td>24</td>
<td>70-95</td>
<td>80-25</td>
<td>Kalle, W. Germany</td>
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<tr>
<td>Tubular</td>
<td>17</td>
<td>88-96</td>
<td>50-30</td>
<td>Wafilin, Holland</td>
</tr>
<tr>
<td>Tabular</td>
<td>13</td>
<td>89-98</td>
<td>45-20</td>
<td>Paterson Candy (PCI), England</td>
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<tr>
<td>Tubular</td>
<td>-</td>
<td>94-97</td>
<td>27-19</td>
<td>United Oil Product, USA</td>
</tr>
<tr>
<td>Flat Plate</td>
<td>0.3-0.5</td>
<td>90-95</td>
<td>75-98</td>
<td>Danish Sugar Corp., Denmark</td>
</tr>
</tbody>
</table>

Source: Glover et al. (1978)
FIG. 1: PRINCIPLE OF THE MULTICHANNEL ELEMENT

SUPPORT

MEMBRANE

CHANNEL

FILTRATE
# TABLE: 3 Commercial Porous Inorganic Membranes

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade Name</th>
<th>Membrane Material</th>
<th>Support Material</th>
<th>Membrane pore Diameter</th>
<th>Geometry of Membrane element</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcoa/SCT</td>
<td>Membralox</td>
<td>AI₂O₃</td>
<td>Al₂O₃</td>
<td>4-100 nm</td>
<td>Monolith/tube</td>
<td></td>
</tr>
<tr>
<td>Norton</td>
<td>Ceradlo</td>
<td>AI₂O₃</td>
<td>Al₂O₃</td>
<td>0.2-5µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NGK</td>
<td></td>
<td>AI₂O₃</td>
<td>Al₂O₃</td>
<td>0.2-5µm</td>
<td>Monolith/tube</td>
<td></td>
</tr>
<tr>
<td>DuPont</td>
<td>FRD-86</td>
<td>AI₂O₃</td>
<td>None</td>
<td>0.06-1µm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Alcan/Anotec</td>
<td>Anopore</td>
<td>AI₂O₃</td>
<td>None</td>
<td>20 nm</td>
<td>Plate</td>
<td></td>
</tr>
<tr>
<td>Jaco Country</td>
<td>Ucarep</td>
<td>ZrO₂</td>
<td>C</td>
<td>4 nm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Dyeing Machine Co.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhone-Poulene/SFEC</td>
<td></td>
<td>ZrO₂</td>
<td>C</td>
<td>4 nm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>DuPont / CARRE</td>
<td></td>
<td>ZrO₂</td>
<td>SS&amp;C</td>
<td>4 nm - 0.1µm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>TDK</td>
<td>Dynaceram</td>
<td>ZrO₂</td>
<td>Al₂O₃</td>
<td>10 nm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Asahi Glass</td>
<td>Glass</td>
<td>None</td>
<td></td>
<td>8-10 µm</td>
<td>Tube/plate</td>
<td></td>
</tr>
<tr>
<td>Schott Glass</td>
<td>Glass</td>
<td>None</td>
<td>10 µm &amp; 0.1 µm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Fuji Filters</td>
<td>Glass</td>
<td>None</td>
<td>4-90 nm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>PPG/SepTech</td>
<td>Glass</td>
<td>None</td>
<td>1.2 µm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Corning</td>
<td>Glass</td>
<td>Cordierite (mullite)</td>
<td></td>
<td>2.6-4.9 µm</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>Toyobo</td>
<td>Glass</td>
<td>None</td>
<td>20 nm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Ceram Filters</td>
<td>SIC</td>
<td>None</td>
<td>0.15-8µm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Fairey</td>
<td>Strata-Pore</td>
<td>Ceramic</td>
<td>Ceramic</td>
<td>1-10 µm</td>
<td>Tube/Plate</td>
<td></td>
</tr>
<tr>
<td>PTI Technologies</td>
<td>SS</td>
<td>None</td>
<td></td>
<td></td>
<td>Tube/Plate</td>
<td></td>
</tr>
<tr>
<td>Mott</td>
<td>SS, Ni, Au, Ag, Pt, etc.</td>
<td>None</td>
<td></td>
<td>0.5-100 µm</td>
<td>Tube/Plate</td>
<td></td>
</tr>
<tr>
<td>Pall</td>
<td></td>
<td>SS, Ni, etc.</td>
<td>None</td>
<td>≥ 0.5 µm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Poretics</td>
<td>Ag</td>
<td>None</td>
<td>0.2-5 µm</td>
<td></td>
<td>Plate</td>
<td></td>
</tr>
<tr>
<td>Osmonics</td>
<td>Hytrex</td>
<td>Ag</td>
<td>None</td>
<td>0.2-5 µm</td>
<td>Plate</td>
<td></td>
</tr>
<tr>
<td>GET</td>
<td>Carbon</td>
<td>None</td>
<td>4 nm - 1 µm</td>
<td></td>
<td>Tube</td>
<td></td>
</tr>
</tbody>
</table>

Table: 4 Characteristics of Carbosep Membranes

<table>
<thead>
<tr>
<th>CUT-OFF</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>M4 membrane</td>
<td>20,000 daltons</td>
</tr>
<tr>
<td>M1 membrane</td>
<td>50,000 daltons</td>
</tr>
<tr>
<td>M6 membrane</td>
<td>2,000,000 daltons</td>
</tr>
<tr>
<td>Water Flux (25°C, 4 Bars)</td>
<td>180-600 1/m² .h</td>
</tr>
<tr>
<td>Burst Pressure</td>
<td>60 bars</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>15 bars</td>
</tr>
<tr>
<td>Crush Strength</td>
<td>30 kgf/20 mm</td>
</tr>
<tr>
<td>Young Modulus Pressure</td>
<td>1000</td>
</tr>
<tr>
<td>pH</td>
<td>0 to 14</td>
</tr>
<tr>
<td>Temperature Membrane</td>
<td>300°C</td>
</tr>
<tr>
<td>System</td>
<td>150°C</td>
</tr>
<tr>
<td>Sterilization</td>
<td></td>
</tr>
<tr>
<td>Oxidant</td>
<td>YES</td>
</tr>
<tr>
<td>Steam</td>
<td>YES</td>
</tr>
</tbody>
</table>

Source: Daniele and Rene (1985)

Table: 5 Carbosep Modules

<table>
<thead>
<tr>
<th>REFERENCE (number of tubes)</th>
<th>DIFFUSING AREA m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 1</td>
<td>0.02</td>
</tr>
<tr>
<td>S 7</td>
<td>0.16</td>
</tr>
<tr>
<td>S 37</td>
<td>0.84</td>
</tr>
<tr>
<td>S 151</td>
<td>3.43</td>
</tr>
<tr>
<td>S 252</td>
<td>5.73</td>
</tr>
</tbody>
</table>

Source: Daniele and Rene (1985)
**Table 6: CERAVER CERAMIC MODULES**

<table>
<thead>
<tr>
<th>Filter Element</th>
<th>Number of filter elements</th>
<th>Length of the element (mm)</th>
<th>Module surface (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multichannel 4 mm</td>
<td>1</td>
<td>850</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>850</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>850</td>
<td>3.8</td>
</tr>
<tr>
<td>Multichannel 6 mm</td>
<td>1</td>
<td>850</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>850</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>850</td>
<td>3.6</td>
</tr>
<tr>
<td>Tubes inner diameter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 mm</td>
<td>1</td>
<td>750</td>
<td>0.0165</td>
</tr>
<tr>
<td>15 mm</td>
<td>1</td>
<td>750</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Maximum operating pressure: 8 bars or, upon request, 25 bars
Steam sterilizable at 130°C.


**Table 7: Mean flux, energy consumption and retention coefficients of different groups of skim milk (Ceraver module)**

<table>
<thead>
<tr>
<th>Particulars of skim milk</th>
<th>Mean initial flux 1/h m²</th>
<th>Mean flux CF⁴ = 4 1/h m²</th>
<th>Mean energy consumption to get CF⁴=4 kWh/m² permeate</th>
<th>Retention coefficients at CF⁴ = 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TS²</td>
</tr>
<tr>
<td>Pasteurised 72°C/15 sec</td>
<td>73.05</td>
<td>52.21</td>
<td>11.94</td>
<td>0.68</td>
</tr>
<tr>
<td>pH: 6.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Severely Heated 95°C/5min</td>
<td>109.89</td>
<td>73.63</td>
<td>8.23</td>
<td>0.722</td>
</tr>
<tr>
<td>pH: 6.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidic 95°C/5 min</td>
<td>106.82</td>
<td>69.47</td>
<td>8.93</td>
<td>0.750</td>
</tr>
<tr>
<td>pH: 6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulated 95°C/5 min</td>
<td>165.40</td>
<td>86.13</td>
<td>7.12</td>
<td>0.729</td>
</tr>
<tr>
<td>pH: 4.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Concentration factor; ² Total solids; ³ Protein; ⁴ Calcium; ⁵ Lactose

Source: Sharma et al (1992)
HARDWARE FOR MEMBRANE PLANT

Dr. R.S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal-132 001

1. INTRODUCTION

An important prerequisite for efficient UF processing is an arrangement for UF membranes and supports that can withstand the pressure used and allow satisfactory performance. The smaller practical unit of this arrangement is termed UF module, where membranes and their supporting structure are housed.

A variety of ultrafiltration equipment designs have been developed. While they differ in the size and shape of the flow channels in which the membranes are housed, they all are designed to control the effects of concentration polarization and to provide sufficient pressure difference across the membranes to enable mass transfer to occur. Additionally, in the processing of food materials, particular attention is also paid to cleaning and sanitization, and materials of construction. (Glover, 1985; Zadon, 1995)

Four basic membrane designs have evolved, as detailed below:

2. TUBULAR

Membrane can be formed on the inside of the tube by pulling a suitably shaped bob vertically upwards through a casting solution contained with the tube. Such membranes typically range from 6 to 25 mm inside diameter and may be cast directly on to a porous support structure, such as a fiberglass-resin tube, which forms the final pressure support. Alternatively, the membrane may first be cast on an intermediate support material which is then inserted into a porous tubular pressure support vessel.

The advantages and its disadvantages of tubular membranes design can be characterized in the following manner (Renner and EL. Salam 1991).

2.1 Advantages

- Capable of handling feed stream with fairly large suspended particles (maximum particle size 10% of the tube diameter).
- Easy to clean by standard CIP systems.
- Individual membrane tubes can be easily replaced on site.

2.2. Disadvantages

- Need efficient pumping generate the high velocity required (> 10,000) Reynolds number.
- High pressure drop
• High energy consumption
• Low surface area/volume ratio.
• High hold up volume
• High floor space required to install the equipment.

3. PLATE AND FRAME

In these designs, membranes are cast in sheet form on to a flat surface which is commonly a porous backing material such as paper or plastic. The function of the backing material can be to provide mechanical support for the membrane during installation, prevent the intrusion of the membrane into the flux channels of the pressure supporting structure and allow the flow of permeate over a small distance towards the location of the permeate flow channels. The membranes or membrane backing material composites are mounted on either side of grooved or porous pressure-supporting separator plates which are designed to channel the flow of permeate away from the membrane. Several such membrane support plate assemblies are mounted in a stack arrangement. Feed material is introduced into the flow channels between adjacent assemblies and permeate is collected from within the support plate.

On evaluating the advantages and disadvantages of the plate and frame configuration the following can be recorded (Madsen, 1977; Renner and EL-Salam, 1991)

3.1. Advantages

• Economic in energy consumption, intermediate between spiral wound and tubular systems
• Operating mainly in laminar flow
• Fairly good performance with viscous solutions
• Low hold up volume
• Minimum floor space is required
• Replacement of membranes on site is relatively easy

3.2. Disadvantages

• Fairly difficult to clean
• Susceptible to plugging

4. SPIRAL WOUND

Spiral wound membranes are typically formed from a "sandwich" comprising two flat sheets of membrane which are separated by a layer of highly porous material and laid on a plastic mesh. The edges and one end of the membranes are sealed with adhesive and the remaining open permeate collection tube, around which the 'sandwiches' are rolled into a spiral. (Glover, 1985; Cheryan, 1986; Renner and Salam, 1991) The membrane assembly is completed by insertion of the roll into a suitable cylindrical housing. In operation, feed is introduced into the tubular housing and flow parallel to the axis of the module within the channel created by the plastic mesh layer, which thereby, acts as both a membrane spacer and a turbulence promoter.
Permeate flows radially through the membrane into porous layer, which acts as a permeate collector.

4.1. Advantages

- Compact, high surface area per volume, minimum floor space required
- Minimum Energy consumption
- Low capital and operation costs
- Low hold up volume

4.2. Disadvantages

- Difficult to process fluids which are high in suspended solids
- High pressure drop, difficult to operate with high viscous solutions
- Mesh spacer, creates dead spots in the flow both, may retain particles
- Faulty membrane elements requires charging the whole module

5. HOLLOW FIBRE

Hollow fibres with internal diameters in the range from 0.5 to 1.0 mm are produced by extruding a polymer solution through an orifice into gelation bath. Modules of this configuration are available from Romicon and Asahi Kasei (Japan). Hollow fibre modules cartridges which contain bundles of 45 to over 3000 hollow fibre. The fibre are oriented in a resin at their ends and enclosed in the permeate collecting tube (Zadon 1995). The feed stream flows through the inside of these fibres and the permeate is collected outside and removed at the top of the collection vessel. The hollow fibre elements are self-supporting capillary tubes with an inside dense skin and inside diameters ranging from 0.5 to 1.4 mm. A special feature of this configuration is the back flushing capacity. (Renner and EL-Salam, 1991).

5.1. Advantages:

- High surface area per volume
- Low hold up volume
- Fair resistance to blockage of the flow channel
- Improved cleanability by back flushing
- Low energy consumption

5.2. Disadvantages:

- Fibres are susceptible to plugging at the cartridge inlet
- Low maximum pressure followed.
- Connection of several elements is limited to parallel configuration.
- Difficult to maintain high flow with high viscous solution in low cartridges.
6. REFERENCES

Figure 1: Principle of ultrafiltration process

- Water molecules (such as lactose, salts, etc.)
- Small mol. wt. solutes (such as proteins, lipids, etc.)
- Macromolecules

Diagram showing the process of ultrafiltration with feed, permeate, concentrate, and membrane components.
Fig. 2 PGI tubular module
Fig. 3 Ronicon hollow fibre UF module.
Fig. 4 Plate and frame UF module

Top: Internal flow of product; 
Bottom: Oval shaped plate membranes and support plate
Fig. 5 Spiral wound UF module
APPLICATION OF NANOFILTRATION IN DAIRY PROCESSING

Dr. A. A. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Since the advent of modern membrane technology more than thirty years ago, reverse osmosis (RO) and ultrafiltration (UF) have established themselves as unique energy-saving concentration and fractionation processes in the dairy industry. The increasing emphasis on broadening of the application of milk constituents, protein in particular, and effective use of milk by-product solids has in recent times brought microfiltration (MF) into focus. And very recently nanofiltration (NF) has become the point of attraction for some specific dairy processing applications. While this novel membrane process has already found place in the dairy industry, much of its potential remains yet to be realized in commercial practice.

2. THE NANOFILTRATION MEMBRANES

The major membrane processes viz. RO working on The principle of mass transfer by diffusion through a semipermeable membrane and UF, employing membranes permitting pore flow are characterized by a big gap between their respective size exclusion ranges: while RO membranes allow only water to pass through thereby concentrating all solids in milk, UF membranes retain fat and proteins but allow all solubles to permeate. Hence earlier there was no membrane alternative of separating soluble salts from lactose and some of the water soluble vitamins. Now nanofiltration (NF) provides selective removal of soluble minerals while concentrating the rest of the milk constituents. NF membranes thus act as ultralight UF membranes and loose or 'leaky' RO membranes. The process is also known as "ultra-osmosis" (a registered trademark of the Filtraion Engineering Co., USA). It is not clear whether the transport mechanism operating in NF is one of mechanical size exclusion or of solution-diffusion (Kelly et al., 1991).

NF membranes, as the name indicates allow permeation in the nanometer size exclusion range which corresponds to the hD (hecto-daltonor dD (deca-dalton) molecular weight range (Jelen, 1991). So, facilitating the separation of mineral ions, NF is essentially a demineralization process for dairy fluids. It employs membranes which are chemically similar to the RO membranes i.e. they are essentially cellulosic or polymeric membranes. In fact, cellulose acetate membranes for RO have earlier been found to show NaCl rejection values of as low as 50% (Kelly et al., 1991). However, presently used NF membranes are usually thin film composites comprising a polyamide barrier layer, a polyester carrier web and a microporous polysulfone support (Gregory, 1987).
The barrier layer formed interfacially on the support by condensation of triesthesyl chloride and piperazine is rich in carboxylate groups. The rejection of salt ion is controlled by anion size and charge. Univalent anions such as chloride, pass relatively freely through the barrier while divalent anions e.g. sulfate, have high rejections. It was reported that the membrane did not differentiate between monovalent and divalent cations (Peterson, 1985) but rejection ratios of the most NF membranes for divalent cations (e.g. Ca) are usually much higher than those for univalent cations (e.g. Na).

Very recently dynamic membranes i.e. membranes formed in-situ on a support e.g. a UF membrane permeated by a process fluid such as whey, milk or a protein solution, have been reported to work in the NF size exclusion range (Obermeyer, 1994). Interestingly, even these membranes allowed permeation of monovalent ions largely in preference to divalent ions such as calcium.

Since the NF membrane permits the passage of mineral ions which contribute to the osmotic pressure in RO, the operating pressures are somewhat lower, usually 10-35 bar, in NF. The temperature tolerance of the NF membrane may vary depending on the make but the usual range is 5-50 °C while the operating pH range is 3-11; however, certain NF membranes have been reported to operate over much wider pH and temperature ranges. (Rautenbach and Groeschl, 1990). The commercially available NF membranes include DRC-1000 (Celfa), Desal-5 (Desalination), HC-50 (DDS), NF-40 and NF-70 (Film Tec), SU-600 and SU-200HF (Toray), NTR-7410 and NTR-7450 (Nitto), NF-PES-10/PP 60 and NF-CA-50 /PET 100 (Kalle), and MB-UO 2540 CXE (MemBrain).

3. APPLICATION IN WHEY AND UF PERMEATE PROCESSING

An overview of NF applications reveals that apparently this technology was evolved specifically for the treatment of whey. Partial demineralization of whey, sweet or sour, and UF permeate from milk or whey has been the most important application of NF primarily aimed at solving the problems of waste disposal and lactose recovery.

3.1 Desalting of salt whey drippings

The whey drippings resulting from pressing of salted cheese curd has a very low value for economic utilization owing to its high salt content. Gregory (1987) employed the NF process for separation of NaCl from Cheddar and Colley cheese drippings. The "salt" whey or "white" whey was concentrated in a commercial-scale NF plant Model 400-118 (Filtration Engineering Co., USA) carrying 18 spiral wound membrane modules with a total membrane area of 177 m², and an operating capacity of 11,000 - 12,000 kg/d of salt whey. The process fluid was concentrated to 60% of the original volume at 43-56°C and 27.6 bar followed by simultaneous diafiltration and concentration to 25% (the diafiltration water being added at half the permeate flux rate) and finally diafiltration at constant volume so as to remove 90% of NaCl. The process resulted in a recovery of 80% whey solids and approx. 83% BOD.

Kelly et al., (1991) reported that there were 10-15 NF plants installed for converting in each plant, 9-22 m³ salt whey into sweet whey per day. The major
benefits from this process were claimed to be through the recovery of whey solids and reduced disposal costs.

3.2 NF processing of sweet whey and UF permeate

Sweet Cheddar cheese whey was processed for partial demineralization in a DDS-Lab-20 unit using HC-50 thin film composite membranes in plate and frame configuration (Guv and Zall, 1992). At an operating temperature of 45°C and pressure of 6 bar, the molar mineral to lactose ratio decreased from 0.28, 0.14 and 0.08 to 0.18, 0.8 and 0.06 for K, Na and P, respectively, when two fold concentration was carried out. However, the ratio remained nearly unchanged for Ca (0.05) and Mg (0.03).

A 64-71% reduction in the chloride-in-dry matter and an overall ash reduction of 25% in Cheddar cheese and rennet casein wheys were achieved by Kelly and Kelly (1995) who employed an APV Pasilac pilot scale HC-50 plate and frame NF plant (4.5 m²) operated at 21-30 bar. At an operating pressure of 25 bar, temperature 21°C and concentration factor 4 (final TS, 22%), the reduction in different minerals was as under (Kelly et al., 1991).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>31%</td>
</tr>
<tr>
<td>Sodium</td>
<td>33%</td>
</tr>
<tr>
<td>Chloride</td>
<td>67%</td>
</tr>
<tr>
<td>Calcium</td>
<td>3%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4%</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>6%</td>
</tr>
<tr>
<td>Ash</td>
<td>25%</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>&lt;3%</td>
</tr>
<tr>
<td>Lactic Acid</td>
<td>27%</td>
</tr>
<tr>
<td>NPN</td>
<td>&lt;0.3%</td>
</tr>
<tr>
<td>Lactose</td>
<td>0%</td>
</tr>
</tbody>
</table>

The permeate flux declined from initial 37.41 l/m².h to 10 l/m².h at a volume concentration ratio of 4 (Kelly and Kelly, 1995b). The partially demineralized whey concentrate was spray dried into a powder with good solubility properties.

UF permeate from whey or milk has also been partially demineralized prior to further processing into lactose and lactose derivatives (Guv and Zall, 1991; Chaudhary et al., 1996). Guv and Zall (1992) concentrated (2x) skim milk UF permeate by using HC-50 membrane in the DDS-Lab unit for NF and found demineralization levels similar to those observed in Cheddar cheese whey; the mineral to lactose ratio decreased from 0.30, 0.15 and 0.095 to 0.19, 0.10 and 0.075 for K, Na and P, respectively, while Ca and Mg remained nearly unchanged. Chaudhary et al. (1996) studied the flux rates during concentration of milk UF permeate (5.25 % TS) in a DDS-Lab 20 unit with 0.288 m² XP-45 membrane at 15-30 bar and 25°C. When a 4x concentration was achieved after 3.5 hours of processing, the flux had decreased from initial 38.3 l/m².h to 8.5-9.1 l/m².h. The ash reduction in the UF permeate was about 27% as against 33-35% in Cheddar cheese whey and 25% in rennet casein whey at similar concentration levels observed by Kelly and Kelly (1995a).

3.3 Dimineralization and deacidification of sour whey

The ability of NF membranes to allow permeation of acids has been exploited for deacidification of sour whey such as that from cottage cheese and acid casein while
at the same time concentrating and demineralizing the fluid (Kelly et al., 1991; Nguyen et al., 1994, Kelly and Kelly, 1995 a,b).

An ash reduction of 35% was obtained after 4x concentration of acid casein whey processed by using HC-50 membrane and it could be increased to 41% by diafiltration (Kelly and Kelly, 1995 a, b). Chloride was reduced by 41.1%. Addition of trisodium citrate as a co-ion increased the permeation of chloride through the so-called "Donnan effect". Losses of lactose and true protein nitrogen amounted to 2.6% and 8.1%, respectively. True protein loss however, increased as the pH was lowered to 3.6. Permeate flux showed a decline similar to that observed with sweet whey (vide section 3.2). Solubility index values for the NF powders from acid casein whey (0.30-0.70) were slightly higher than those obtained for conventional spray dried powders and whey protein concentrates (0.25-0.30)

Sachdeva et al. (1994) and Patel et al. (1994) examined the performance of AFC-30 and AFC-20 NF membranes (PCI, UK) for demineralization of acid casein whey from cow and buffalo milks. The AFC-30 membrane showing high rejection values for phosphorus (98 and 96%), calcium (99 and 99%), chloride (96 and 96%), potassium (92 and 94%) and sodium (92 and 94%) for cow and buffalo wheys was rather ineffective in bringing about any appreciable demineralization of the two types of whey. On the other hand, the AFC-20 membrane was found to be effective in partial demineralization of the acid casein whey from buffalo milk, the retention of phosphorus, calcium, chloride, potassium, sodium, magnesium and citrate being 60.0, 53.8, 66.7, 41.5, 48.3, 55.0 and 56.5%, respectively. The mean flux rate observed was 40.3, 45.8 and 53.9 l/m² h at 30, 40 and 50°C, respectively. Clarification of whey improved the permeate flux by 15%. The flux rate was higher (66.5 l/m² h) at pH 3.33 (VCR, 3.15). However, the AFC-20 membranes performance appeared to deteriorate over a period of time as indicated by increased solids losses (from initial 0.2 to 1.2%) in the permeate after 50 operational runs of 5 h duration each (Patel et al., 1994).

Since the fluid pH is an important parameter influencing the performance of the NF membrane, acid casein whey behaves slightly differently as compared to rennet casein and cheese whey as shown in Table-1 (Kelly et al., 1991). Acid casein whey exhibited an ash retention level intermediate between those for the other two types of whey, but lower chloride reduction upon concentration by HC-50 membrane to a VCR of 2 or 4. The difference in initial mineral concentration of the different wheys might also be partly responsible for the observed differential mineral removal.
Table-1: Extent of removal of ash and chloride from different types of whey concentrated by NF (HC-50 membrane)

<table>
<thead>
<tr>
<th>Type of whey</th>
<th>pH</th>
<th>VCR</th>
<th>Reduction of ash in DM</th>
<th>Chloride reduction before dialfiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Before dialfiltration (%)</td>
<td>After dialfiltration (%)</td>
</tr>
<tr>
<td>Acid casein</td>
<td>4.60</td>
<td>2</td>
<td>18.2</td>
<td>28.4</td>
</tr>
<tr>
<td>Acid casein</td>
<td>4.60</td>
<td>4</td>
<td>32.8</td>
<td>41.2</td>
</tr>
<tr>
<td>Cheddar cheese</td>
<td>6.29</td>
<td>2</td>
<td>18.5</td>
<td>31.0</td>
</tr>
<tr>
<td>Cheddar cheese</td>
<td>6.29</td>
<td>4</td>
<td>35.2</td>
<td>42.4</td>
</tr>
<tr>
<td>Rennet casein</td>
<td>6.72</td>
<td>2</td>
<td>13.6</td>
<td>22.8</td>
</tr>
<tr>
<td>Rennet casein</td>
<td>6.72</td>
<td>4</td>
<td>25.8</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Kelly et al., (1991)

3.4 NF concentration of whey for lactose manufacture

Partial demineralization of whey meant for lactose production has been associated with improved lactose yield as demonstrated by Guv and Zall (1992). These authors found the gross yield of lactose crystals from sweet whey concentrated by NF to go up from 62.35% at concentration factor (CF) of 1.0 to 70.47% and 72.58% at CF of 2.0 and 3.0, respectively. The corresponding values for skim milk UF permeate were 61.69, 66.26 and 69.48%. These increases were attributed to depletion of minerals especially monovalent cations such as sodium and potassium through nanofiltration. The two processes of concentration and partial demineralization going on simultaneously during nanofiltration make this membrane process particularly valuable for lactose manufacture from whey or UF permeate. According to Kelly et al., (1991), concentration of whey (or milk) UF permeate by NF prior to the manufacture of lactose has been carried out at 3 or 4 commercial plants. The advantages accruing from the process include reduced costs of condensing before crystallization and reduced cost of crystallization, the latter because of higher yields obtained and less washing required.

3.5 Economics of demineralization of whey by NF

While it is recognized that high level of demineralization of whey or UF permeate would necessitate the use of electrodialysis (ED) or ion exchange, partial demineralization by NF could under certain circumstances be preferable to other processes. Based on a case study involving casein whey produced by hydrochloric acid precipitation of skim milk (275,000 kg whey/day). Kelly et al., (1991) concluded (Table 2) that NF is the lowest cost option if a demineralization level of up to 32% ash removal is to be obtained. Such demineralization levels would be required, for instance, for upgrading of acid whey into sweet whey. When demineralization to the
extent of 62% is to be achieved, preconcentration by NF to obtain 32% demineralization prior to ED to the final demineralization level would result in capital saving of approx. 25%. Preconcentration of whey to about 20% TS is in any case required for ED. Hence NF providing partial demineralisation while concentrating the whey may, under certain situations, be preferred to evaporation or RO to attain the required solids level. The authors further concluded that an existing ED plant may be expanded by addition of the NF at the pretreatment stage, the latter thus being one of the options to be considered to increase the throughput.

Table 2. Estimated costs of electrodialysis (ED) of acid casein whey 275000 kg/year for different levels of demineralization

<table>
<thead>
<tr>
<th>Level of demineralization by ED (%)</th>
<th>ED membrane area required (m²)</th>
<th>Approx. yield % of feed solids</th>
<th>Capital cost of ED plant (US $)</th>
<th>Operating $/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 → 32</td>
<td>120</td>
<td>93</td>
<td>400 000</td>
<td>470</td>
</tr>
<tr>
<td>0 → 62</td>
<td>200</td>
<td>86</td>
<td>555 000</td>
<td>82.5*</td>
</tr>
<tr>
<td>32 → 62</td>
<td>130</td>
<td>92</td>
<td>425 000</td>
<td>51.5</td>
</tr>
<tr>
<td>0 → 90</td>
<td>430</td>
<td>75</td>
<td>1 300 000</td>
<td>188*</td>
</tr>
<tr>
<td>32 → 90</td>
<td>320</td>
<td>80</td>
<td>1 100 000</td>
<td>147</td>
</tr>
</tbody>
</table>

* Does not include the cost of preconcentration necessary for ED.

4. THE POTENTIAL OF NANAOFILTRATION IN OTHER DAIRY PROCESSING APPLICATIONS

Besides whey treatment, other potential applications of NF may be considered for improved dairy processing operations. Such applications include treatment of cheese brine for extending its useful life and/or preserving its initial performance while solving the disposal problem (Kelly et al., 1991). However, NF is faced with UF and MF as the competing processes in this regard. Another potential application of NF is demineralization of lactose, the mother liquor or "delactosed" whey/UF permeate. Since this waste product from lactose manufacture is already in a concentrated form, dilution and dialfiltration with NF can be used to partially demineralize and upgrade its quality for animal feed purposes as suggested by Kelly et al., (1991).

Removal of part of soluble salts from milk can potentially improve its heat stability characteristics. Such an application of NF might be very useful in respect of UHT-sterilized milk concentrates. As demonstrated by Patel et al., (1993) employing a combined UF-RO process for the production of a long life concentrate, reduction in the concentration of soluble salts in milk can not only enhance the stability during UHT processing of the concentrate from it, but also extend the gelation-free life of the product.

However, for the NF process to be useful in this regard, it should permit appreciable removal of divalent cations viz. calcium and phosphate alongwith the monovalent ions. Unfortunately few NF membranes are effective in separation of divalent ions. An NF membrane permitting the passage of divalent ions would also
enable treatment of buffalo milk which, primarily owing to its high calcium content, yields chhana with a hard body and coarse texture less suitable for making chhana sweets than that from cow milk (De, 1980; Sindhur, 1993). Similarly, buffalo milk may be made more suitable for the production of hard cheese varieties such as Cheddar and Gouda if its calcium concentration is reduced through NF, since its high calcium content is believed to be responsible for the body and texture defects in the product.

Partial demineralizations of milk, apparently achievable by NF, might also be valuable for the manufacture of infant milk food, since the normal mineral content of bovine milk is in excess of the baby's requirement (Singh and Mathur, 1989). NF membranes selectively excluding monovalent ions such as Na+ and retaining most of the divalent ions e.g. Ca2+, may be employed for mineral modification of cow milk, whose calcium content is somewhat lower than desired for preparation of good quality paneer as shown by Singh and Kanayvja (1988) who added calcium chloride to cow milk before coagulation for paneer-making. Along similar lines, there exists a significant potential for NF concentration of cow milk for khoa production, as not only normal cow milk khoa lacks in texture as compared to buffalo milk khoa but it also has a salty taste (De, 1980).

5. CONCLUSION

Nanofiltration (NF) has recently emerged as a membrane processing technique offering the possibility of concentrating dairy fluids such as whey and milk while at the same time effecting partial demineralization. It has been established that this technique can be profitably used for demineralization of whey to the extent of 30-32% for various purposes such as lactose manufacture. NF processing of whey and UF permeates offers an opportunity to mitigate the problem of their disposal as it greatly reduces the BOD of these by-products. There exists a considerable potential of NF processing of milk using selective membranes for partial mineral removal aimed at improving the quality of certain indigenous milk products such as chhana from buffalo milk, and paneer and khoa from cow milk. Hence research attempts need to be made in this direction. NF concentration of milk meant for UHT sterilization also needs to be investigated for its potential to enhance the heat stability and resistance to age gelation of the concentrate.

6. REFERENCES


ELECTRODIALYSIS PROCESS AND ITS APPLICATION IN WHEY DEMINERALISATION

Dr. Vijay Kumar Gupta
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Electrodialysis is a separation process in which membranes are used to remove ionic (electrically charged) species from non-ionic species. Electrodialysis is employed in dairy industry to demineralise whole whey and other milk derivative solutions.

2. SALIENT FEATURES OF ELECTRODIALYSIS

The key to the electrodialysis process is the use of ion-selective membranes. These membranes are essentially ion exchange resins cast in sheet form. Ion selective membranes that allow passage of positively charged cations (Na⁺, K⁺) are called cation membranes. Membranes that allow passage of negatively charged ion (Cl⁻, PO₄³⁻) are called anion membranes.

To achieve separation by electrodialysis, cation and anion membranes are altered with plastic spaces in a stock configuration with positive electrode (anode) at one end and cathode at other end. When a DC voltage is applied across the electrodes, electrical potential created causes anions to move in the direction of anode and cations towards cathode. The ion-selective membranes form barrier to ions of opposite charge. The result is: anions attempting to migrate to anode will pass through anion membranes and are stopped by cation membranes; cations trying to migrate to cathode pass through cation membranes but are stopped by anion membranes. Hence, members form alternate compartments of ion-diluting cells and ion-concentrating cells. By circulating whey through diluting cells and brine solution through concentrating cells, free mineral ions leave the whey and collect in brine stream.

Level of demineralisation depends on (i) initial ash content, (ii) current density and (iii) duration of time the solution of whey is within the cells.

3. ELECTRODIALYSIS MEMBRANES

Electrodialysis membranes are thin sheets of cation or anion exchange resins, usually reinforced with synthetic fibres necessary to give mechanical strength. Most commercially available membranes are having effective pore sizes of 0.7-2 nm, which are slightly greater than atomic dimensions and therefore, impermeable to flow of liquids and solids and to diffusion of large molecules.

Membranes are composed of a styrene divinyl benzene resin background. For cation exchange membranes, sulphonic acid groups constitute usual substituted exchange sites. Anion exchange membranes have quaternary ammonium or tertiary
amine compounds as ion exchange sites. Saran and Dynal are usual backing materials employed.

Parameters of importance in characterising membrane properties are electrical resistance, permeability, selectivity, ionic capacity, solvent transfer and resistance to chemical attack. Monovalent ions are more mobile than divalent ions.

4. ELECTRODIALYSIS PLANT

For a two membrane stack system, stacks are connected in series with internal circulation over each stack. The salt-uptaking process water must be continuously removed or renewed with a feed and bleed system. It also needs continuous acidification with HCl in order to compensate for alkalization during the process. The process water requires preheating to operating temperature. 2-5 m³ of water per m³ of whey (6% DM) is used, depending on demineralisation rate.

Electrodialysis plant can be run either continuously or in batches. A batch system, which is often used for demineralisation rates above 70%, can consist of one membrane stack over which process liquid, e.g., whey is circulated until a certain ash level is reached. This is indicated by conductivity of process liquid. Holding in batch system can be as long as 5-6 hours for 90% demineralisation at 30-40°C, pre-concentration of whey to 20-30% DM is desirable for better capacity utilisation and lower electrical power consumption. Whey concentrate should be clarified before processing through electrodialysis unit.

In a continuous plant, consisting of five membrane stacks in series, holding time can be reduced to 10-40 minutes. Maximum rate is often limited to 60-70%. An electrodialysis plant can easily be made automatic and supplied with a CIP system. Cleaning sequence include water rinse, alkaline solution cleaning (pH 9), water rinse, cleaning with HCl (pH 1) and final water rinse.

A typical industrial electrodialysis stack for demineralisation of whey employ about 200 pairs. Each membranes has an effective area of 0.5 m², giving a total of 50 m² per stack. An actual process for demineralisation by electrodialysis begins with pasteurisation of whey and concentration to 28% TS. Concentrated whey is clarified to remove any insoluble protein and fines and then passed through the electrodialysis stack. For batch operation, process times of 3.5-6 h are typical, depending on operating temperature (35-45°C) and for continuous operation, low temperatures (12-20°C), short residence times (10-30 min.) are there. After demineralisation, whey is further concentrated by evaporation to 55% solids and spray dried.

5. DEMINERALISATION OF WHEY AND UF PERMEATE

The high mineral content of whey and permeate is a factor greatly limiting the applications for feeding and food ingredient purposes. Electrodialysis is, of course, not the only technique available for producing demineralised whey. Other methods include ion exchange, ultrafiltration and nanofiltration. Ion exchange is widely used for whey demineralisation; however, the process has a number of disadvantages, including potential denaturation of proteins due to low pH in cation column and loss of protein in
anion column. Ultrafiltration can also be used to produce demineralised whey protein. However, since whey protein based infant formula requires both whey proteins and full amount of lactose present in whole whey, ultrafiltration which removes lactose along with ash, does not provide same direct route to product as does electrodialysis. In general, economics favours a single step process removing ash from protein and lactose as opposed to a two step process.

The first commercial electrodialysis demineralisation plant for whey began operation in 1961 in Wisconsin. In the last 20 years, a number of other manufacturers followed low mineral whey in the premium products. Presently, there are 45-50 dairy plants world-wide with electrodialysis systems. Ionics alone had installed over 40 electrodialysis lines for whey demineralisation around the world. There are number of plants with installed capacity to demineralise 500,000 kg or more of fluid whey. Total world-wide electrodialysed production is estimated at 150,000 MT of reduced mineral whey solids (dry basis). Classical electrodialysis process with anion/cation membranes have the following problems, as a consequence of membrane fouling, associated with them:

- deposition of calcium phosphate on the cathode side of the cation-selective membrane. This deposition can be removed by a normal cleaning process using acid.
- deposition of denatured, negatively charged protein molecules which pass through the membranes and are deposited as a thin film in the membrane pores. At a current density of 20-25 mA/cm², and with continuous operation, there is a danger of irreversible protein deposition.

Effective cleaning of the anionic membranes can only be achieved by washing with alkaline solutions. As a consequence, however, of the alkaline effect, the life span of the anionic membranes is shorter than that of cationic.

As per Sienkiewicz and Rieder (1990), a demineralisation optimum for the electrodialysis of whey is achieved at pH 4.65. This pH value lies close to the isoelectric point of whey proteins, at which their net charge is approximately zero. Electrodialysis laboratory trials have demonstrated that at current densities of 6-8 mA/cm², an enhanced demineralisation effect, of up to 72% in 4 hours, is achieved. The temperature of the whey increases during the electrodialysis from 22-30°C to 41-48°C. Salt concentrations which are too low cause an excessive electrical resistance in the whey and thereby increase the energy consumption of the process. For this reason, the dry matter content of rennet whey is adjusted, for demineralisation, to 18-20%. For a 50% demineralisation by electrodialysis, a consumption of 10-28 KWh of electrical energy must be considered for each kg of demineralised whey powder. The effluent of an electrodialysis plant processing 60,000 tons of liquid whey contains about 300 t organic matter.

An investigation (Singh and Mathur, 1989) was undertaken to study the influence of electrodialysis process variables (concentration of salts in stream, flow rate of brine, feed concentration, membrane area and voltage) on the demineralisation of skim milk, rennet whey and 15: 85 skim milk : whey mixture concentrated to 28 and 35% TS. Mineral content of skim milk decreased steadily (P < 0.01) with increase in surface area of membrane from 0.3 to 1.5 m² and rate of demineralisation was greater
(p<0.01) with 0.6% than with 1.4% brine in depleting stream. Extent of demineralisation increased with voltage up to 3 V, with feed concentration upto 35% TS and with flow rate upto 90 l/h. Optimum conditions recommended for obtaining 50% demineralisation of rennet whey (35% TS) using a membrane of surface area 3.6 m² are: a flow rate of 90 l/h and electrical potential of 3 V in 0.6% brine.

Concentrated buffalo rennet whey (35% TS) was subjected to electrodialysis using 0.6% brine in depleting stream, feed rate of 90 l/h, and voltage 3 V (Singh and Mathur, 1990), diffusion rates of Cu, Mn and Zn were not affected by surface area between 0.6 and 3.6 m² but rate of diffusion of other 5 minerals increased (p<.01) with surface area in order of K>Na>Ca>Fe>P. At 50% demineralisation, 92.88, 73.20, 36.81, 29.11 and 27.25% of minerals were depleted in skim milk, while 68.21% of K, 50.34% of Na, 33.49% of Fe, 32.51% of Ca and 26.73% of P were depleted in whey.

In an experiment, lactic casein whey and sulphuric acid casein whey, deproteinized by ultrafiltration, were concentrated to about 20% TS by reverse osmosis and subsequently demineralised to 2% ash (solid basis) by electrodialysis. Progressive increase in pH of acid wheys from 4.5 to 6.0 during demineralisation is there. Utilisation of permeate stream, derived from production of soluble whey proteins by ultrafiltration, remains a major problem. Deproteinised whey can contain 5-13% minerals on a solid basis. So, some degree of mineral reduction is required in order to utilise it in baby foods. Ultrafiltration of whey at pH 6.0 results in reduction in mineral content in permeate due to partial rejection of calcium phosphate at the membrane.

Analytical results showed that deproteinated cheese whey with a mineral content of 2% (on solids basis) contained 70% of residual ash as calcium and inorganic phosphate. Preconcentration using RO had resulted in reduction of lactic acid/lactate by 35-40%. In conclusion, it would appear that electrodialysis offers an alternative to ion exchange as a means of demineralising deproteinated whey. Due to relative selectivity of electrodialysis, with pre-concentrated feed, in removing monovalent ions, some specificity, during demineralisation can be achieved. Exhaustive demineralisation is uneconomical.

6. UTILISATION OF DEMINERALISED WHEY

1. Electrodialysis products are often offered as a base for humanised milk. Approximately 65% of total reduced-minerals whey is used to manufacture infant-formulae simulating human milk. For this application, around 90% demineralisation is required.

2. Europe utilises 25,000 tonnes of electrodialysed whey solids annually in the production of demineralised calf milk replacers.

3. Demineralised sweet whey (25-65% demineralised) can be used in dietetic food as well as foods such as coffee whitener, soft serve ice cream, milk shakes, whey drinks and caramel, citrus drinks, salad dressing, animal feeds, bakery goods, confectionery coatings and dry mixes.
4. 35-50% demineralisation of acid casein whey gives a product which has a mineral and salt composition comparable to sweet whey and is used in the manufacture of dried whole sweet whey.

5. In USA, cottage cheese whey is demineralised to reduce effluent costs.

6. Reduced mineral whey is used as a less expensive substitute for non-fat dry milk.

7. Ultrafiltration permeate may also be demineralised by electrodialysis to increase lactose yield in crystallisation.

8. Although usage of reduced mineral whey in food processing products is small in comparison to usage of whole whey powder, there are a number of applications for which the lower overall ash content, or the lower level of a specific ion such as sodium is desirable. For 50% demineralised Cheddar cheese whey, the loss of Ca is about 20% while the reduction in sodium and Cl are about 50% and 90% respectively.

7. REFERENCES

MEMBRANE FOULING - PROBLEM AND TREATMENT

Dr. R.S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

A major limiting step in the use of pressure driven membrane process especially with multicomponent feed streams is fouling of membranes. Fouling is generally attributed to the accumulation of macromolecules such as protein, lipids or inorganic salts, on the membrane surface and to the possible crystallization and precipitation of smaller solutes that are normally permeable such as sugar and salts, in membrane pores. (Maubois 1980, Merin and Cheryan, 1985, Patel and Reuter, 1985). The fouling of membrane is generally considered an irreversible phenomenon. The decline in flux is rapid at the initial stage and slower in the later stage.

The decline in flux is also due to concentration polarization. During ultrafiltration process water is removed from the system, due to which the solute concentration near the membrane increases (Glover, 1985; Patel and Reuter, 1985b; Cheryan, 1986). This results in a lower flux due either to increased hydrodynamic resistance or to higher local osmotic pressure decreasing the driving forces. Thus the flux will then be influenced by those factors affecting the rate of mass transfer of the solute back from the membrane surface to the bulk fluid. Reported means of minimizing the fouling problem include increasing turbulence near the membrane by increasing flow velocity or by use of turbulence promoters, and adjusting the operating pressure to the optimum for the system (Cheryan, 1986, Jayaprakasha et al., 1995).

Fouling is a serious problem in all UF processes. It has several implications which are connected with: (Renner and El-Salam, 1991)

- energy consumption; more energy is needed in different ways to compensate the fouling effect
- duration of continuous operation of the UF plant without the need for cleaning; rapid fouling shortens the operation period
- membrane durability
- properties and quality of concentrate; this is important in batch UF where increased fouling increases the holding time of fluid in the system which increases its microbial load. In other words, fouling will affect the overall economy of a UF plant.

Generally, the fouling phenomenon is extremely complicated and in several aspects is not fully understood. Several theories have been proposed to explain this flux decline. Most of these theories are based on the solute properties and its flow conditions above the membrane surface.
2. TYPES OF MEMBRANE FOULING

In practice we have to distinguish between two types of membrane fouling:

Surface (temporary) fouling: Here, foulant appears as an evenly deposited layer on the membrane surface. This type of fouling can be easily removed by cleaning solutions. Therefore, the permeation rate of the fouled membrane can be generated by cleaning. This is the most common fouling observed in UF plants. Most of the studies on membrane fouling have dealt with this type of fouling.

Pore (permanent) fouling: In this type of fouling particulate matter diffuses into the membrane, blocking the pores of the separation layer of the membrane. The fouling is characterized by an uneven distribution of the foulant and compression of the separation zone. The flux of the fouled membrane cannot be regenerated by cleaning. This type of fouling determines the lifetime of the membrane. Fouling of this type has received much less attention. It is mainly dependent on the treatments received during day-to-day operation and in particular the quality of the cleaning water. Shutting down the UF system during operation and leaving the treated fluid in contact with membranes for 1-2 min results in severe fouling (Renner and El-Salam, 1991).

The following theories have been proposed to explain membrane fouling:

2.1. Concentration polarization

According to this theory flux reduction is not attributable to plugging of the UF membrane, but rather to the formation of a gel layer on the membrane surface when the concentration of the fluid stream adjacent to the membrane surface reaches the solubility limits of the impermeable solutes. At this stage the transmembrane flux is entirely dependent on the resistance of this gel layer and the back diffusion of the macromolecules in the concentration boundary layer.

2.2. Adsorption of macromolecules to membrane surface

One of the important factors involved in membrane fouling which has been neglected in previous theories is the adsorption of macromolecules on the membrane surface. It is well known that macromolecules have a strong tendency to adhere to almost any interface. Adsorption at the solid-liquid interface is a very complicated phenomenon, but it is dependent on solution properties (pH, ionic strength, and concentration of solutes) and surface characteristics (hydrophobicity and surface charge). Exposure of membrane surface to concentrated protein solutions or milk with no transmembrane pressure or flux and subsequent washing of the membrane significantly decreases the flux of pure solvents. The adsorption of macromolecules to the membrane surface is a thermodynamically spontaneous process and is probably the first step in fouling (Barbano et al., 1987).

2.3. Sequestration fouling reactions

According to this theory, fouling occurs in four distinct stages. A mathematical model was given to express the sequence of a concentration polarization layer; this
stage lasts for less than 5 seconds followed by adsorption of proteins on the membrane surface. The third stage comprises a protein polymerization reaction to a gel which is a first order reaction. The fourth stage is another protein polymerization reaction of different reaction order.

3. MEMBRANE FOULING IN THE DAIRY INDUSTRY:

Membrane fouling in the dairy industry arises from two sources:

- the composition and properties of the treated fluid;
- the quality of the cleaning water used.

Apart from the extensive literature on membrane fouling during UF of whey limited information is available on membrane fouling during UF of whole and skim milk, buttermilk or coagulated milk.

3.1. Membrane fouling during ultrafiltration of whey

The term whey is misleading in discussing its behaviour during the UF process. In fact, there are several effluents arising from the manufacture of different types of cheese and casein. Each of these effluents has its characteristics composition and quality. However, two major types of whey can be distinguished (Hayes, 1974; Kuo and Cheryan, 1983).

- Sweet whey, which arises from rennet-coagulated cheeses and usually is characterized by a pH higher than 5.0 and a low calcium content.
- Acid whey, which arises from acid-coagulated cheeses (e.g. Cottage cheese) and from casein manufacture; it is characterized by a pH less than 5.0 and high mineral contents especially calcium phosphate.

Several variations of sweet whey occur depending on the treatments received during cheesemaking as is apparent from the fat losses in whey.

The type of acid used in casein precipitation (lactic acid, HCl, H₂SO₄) has a determinant effect on the solubility of the mineral constituents of acid whey which directly affect membrane fouling. In the case of lactic acid whey, starters are usually used to develop the desired acidity. In this case, part of the lactose is converted into lactic acid and a small part of the protein is broken down.

Another aspect is that whey is usually stored for some time before processing without any heat treatment. This allows microbial growth, and changes in the composition and properties of whey, especially pH. Bacterial cells can also be considered as additional membrane foulants arising in whey during storage.

Generally, the following components participate in membrane fouling during UF of whey: proteins, inorganic constituents and lipids.
Protein:
These have a greater influence on the flux of UF membranes than small molecular weight solutes present in whey. However, there is a lack of agreement between different studies on the role of a specific protein in membrane fouling (Peri and Dunkley, 1971; Patel, 1985; Cheryan, 1986).

1. The fouling is considered as a complex network of several proteins. The scanning electron microscopy of layer suggests that fouling occurs when the large whey constituents including microorganisms settle on the membrane in a lattice network which fills in and is coated over with small sheet-forming proteins such as β-lactoglobulin.

2. It is known that α-lactalbumin to have the strongest gel-forming tendencies and bovine serum albumin the least, while β-lactoglobulin has the worst long-term fouling effect during UF of whey.

3. The glycomacropeptide arising from the action of rennin on k-casein is considered as a major foulant contributor in sweet whey.

4. The permeation rate of cheese whey generated from milk coagulated with Mucor pusillus protease was reported to be higher than that generated with calf rennet. A membrane foulant from calf rennet whey contained a prominent component of approximately 10 000 daltons that was not observed in membrane foulants from Mucor pusillus whey.

5. Casein fines and incompletely rennet-coagulated casein in whey contribute to fouling, therefore, fresh whey is often much more fouling than a whey which has been stored for 1-2 h.

Inorganic constituents:
The studies (Hayes et al, 1974) showed that the permeation rate during UF of acid casein whey is on average only 60% of the permeation rate obtained with Cheddar cheese whey. The impaired permeation of acid whey has been attributed to its high Ca content which is twice as much as in sweet whey. Calcium is present in whey in two forms, a permeable and an impermeable fraction. The latter is present as colloidal phosphate and attached to the β-lactoglobulin of whey. When the concentration of calcium phosphate in whey retentates exceeds its solubility index, it tends to crystallize forming deposits as a specific membrane foulant. Increasing the Ca content of cheese whey to the level of Ca in casein whey at pH values around 6 increases the fouling of UF membranes. The severity of fouling is greatest if the method for pH adjustment favours the precipitation of calcium phosphate in the gelatinous apatite form. The role of Ca in membrane fouling was studied. Calcium was reported to produce considerable hardening of the deposited layer which is further enhanced by an increase in the pressure. A high Ca content and high pressure lead to the formation of a layer on the membrane which adheres so strongly that it can hardly be removed by washing with water. It has been studied that residual casein interacts with calcium phosphate in whey resulting in membrane fouling during UF. It was also reported that phosphate present in whey in high concentration can bind to the membrane and serve as a locus for binding other constituents.
Lipids:
Small milk fat globules and fat globule membrane materials are found in whey and can hardly be removed by centrifugation. These constituents found to be one of the foulants in whey during ultrafiltration (Cheryan, 1986).

3.2. Membrane fouling by the cleaning water

The quality of water used for cleaning the UF equipment is of great importance to membrane fouling for the following reasons:

Presence of suspended particles:
Very small particles (10^{-8}-10^{-6} m) can easily form deposits on the membrane surface. These particles are generally difficult to remove once they are deposited on the membrane surface. Therefore, it is recommended to prefilter the water used in UF plants through 2 μm filters in order to remove any suspended particles present.

Presence of high levels of calcium and heavy metals:
Iron has been shown to be the main factor present in the cleaning water which affects membrane fouling (irreversible) and to be responsible for the long-term decrease of flux in UF plants. When two plants are compared, one using prefiltered water and the other one water treated with ion exchange resins, a more rapid membrane fouling was reported in the first plant. As a recommended specification the level of Fe, Mn, Al₂O₃, and SiO₂ in the cleaning water should be less than 0.05 ppm.

Electron microscopy has been used to study fouled membranes from UF plants processing acid casein whey. The surface deposits contained aluminium, silica, iron and traces of calcium.

Calcium phosphate is one of the important foulants in the dairy industry. UF temperatures higher than 50°C enhance precipitation of calcium phosphate on UF membranes. One of the purposes of cleaning is to remove calcium phosphate from the membrane surface. The presence of Ca concentrations in the cleaning water would risk the formation of calcium deposits during the cleaning of the plant.

Presence of humic acids:
These may be a serious problem for UF plants using cleaning water containing humic acids that escaped from the filters used in the purification of this source of water. Humic acids can be removed from the cleaning water by using 2 μm filters.

Presence of chlorine:
Chlorine is used in some areas for treating potable water. Usually traces of chlorine are present in this water source. Although most of the commercial membranes available in the market withstand the presence of chlorine, some are affected especially those made from cellulose acetate, and polyamide.

Treatment of cleaning water:
Cleaning water used in UF plants should be subjected to careful treatment depending on the quality of the available source of water. Most of the commercial UF equipment producers recommend prefiltration of the cleaning water through 0.2 μm filters.
filters. However, an additional ion exchange treatment is needed in most cases. The conductivity of the water after these treatments should not exceed an electrical conductivity of 30 nmmhos.

4. EFFECT OF OPERATION PARAMETERS ON FOULING

The formation of the fouling layer is controlled by the rate at which a solute can be transferred from the membrane surface back into the stream and the degree of compaction of the gel layer formed (Glover, 1985; Cheryan, 1986; Renner and El-salam, 1991).

4.1. Flow Rate

Generally, higher shear rates at the membrane surface are very important factor in combating membrane fouling, as thereby the deposited materials are continuously removed and thus the hydraulic resistance of the fouling layer is reduced. The different methods used to generate the high shear rate needed are:

- Increasing the flow rate of the circulated stream; it has to be realized that this requires high pumping costs and more energy consumption per unit permeate removed;
- Decreasing the flow channel dimensions;
- Insertion of a static mixer, turbulence promoter, or hermetic pulses; several devices have been described and evaluated; however, the use of these devices has been limited to experimental work; the convection-promoter devices generally suffer from increased flow resistance which may be quite significant at high Reynolds numbers.

4.2. Temperature

The effect of temperature on fouling can be understood from its effect on the properties of the feed stream. Increasing the temperature results in a decrease in the viscosity of the processed fluid which in turn increase its rate of flow especially in concentrated fluids with non-Newtonian behaviour. In the mean time, high temperature increases the solute diffusivity and the rate of transport of solutes from the membrane surface into the bulk stream. The high flux at a high operation temperature manifests the role of temperature in combating fouling. However, overheating will induce fouling by decreasing the solubility of calcium phosphate and increasing heat denaturation of whey proteins. generally, increasing the temperature in the range used in UF of milk and whey (30-50°C) has a beneficial effect on reducing fouling.

4.3. Pressure

According to the concentration polarization theory, the flux increases with the increase of applied pressure until the gel formed reaches a concentration limit where flux becomes independent of pressure. further, increase in applied pressure results in a temporary increase in flux; however, this pressure increase raises the driving force for UF but does not affect transport of solutes back into the bulk stream. Consequently, a thicker and denser gel layer is formed which reduces flux until it reaches its initial
steady state. Increasing pressure over a critical point results in a lower flux due to the compaction of the gel layer formed and the increased hydraulic resistance.

5. REGENERATING MEMBRANE PERMEABILITY

After a certain period of continuous operation, the flux of the UF membrane reaches a minimum, and the system needs cleaning. The duration of the period of continuous running without the need for cleaning is dependent on the following factors:

- the type of membrane and its configuration.
- the operation conditions (flow rate, pressure, temperature)
- the composition and properties of the processed fluid.

Cleaning is the treatment that regenerates the membrane permeability. Efficiency of cleaning is usually measured by determining the recovered percentage of the original flux (not less than 95%). Therefore, selection of the cleaning agents and conditions is of great importance. They should meet the necessary efficiency and should not affect the membrane or equipments.

The first step of the cleaning cycle is rinsing with water followed by the cleaning solutions. The importance of the rinsing step becomes apparent from the finding that up to 98% of the deposited layer can be removed during this step depending on the velocity of the rinsing water. Therefore, rinsing should be carried out at high shear stress and low transmembranes pressure.

Agents used in cleaning can be classified into three categories:

- **Strong alkanals and acids.** Usually sodium hydroxide and nitric/phosphoric acids are used in the cleaning of dairy equipment. These are also the most simple agents to be used for UF plants as a common practice in dairy factories. Alkali affects the solubilization of proteins in the foulant deposits, while the acids mainly affect solubilization of minerals.
- **Proteolytic enzymes.** These assure solubilization of protein aggregates and deposits, which are difficult to remove, through effective hydrolysis of these deposits and formation of soluble degradation products.
- **Detergents,** which can remove both protein aggregates and lipids present in the deposits by forming detergent-protein complexes and emulsifying the lipid materials.

6. REFERENCES


TECHNOLOGY OF UF-CHHANA

Mr. D. K. Sharma
Dairy Technology Division, NDRI (ICAR), Karnal - 132001

1. INTRODUCTION

Chhana is an Indian 'heat-acid' coagulated soft cheese. It serves as a base material and filler for a large variety of Indian sweet meats. It has a creamish white colour, soft and spongy body and granular texture. It has sweetish acidic flavour. Cow's milk is most suited for chhana (De and Ray, 1954; Date et al., 1958) however, attempts have been made to make good quality chhana from buffaloe's milk (Jaglan et al., 1960; Kunda and De, 1972). The existing technology of chhana making is simple. Cow's milk is heated to boiling point and then cooled to 70°C before the coagulant addition. The coagulant (sour whey, dilute lactic acid or citric acid) is generally added with constant but slow stirring, till coagulation is complete. The coagulum is allowed to settle, and the whey is drained off. The coagulum is collected in a cloth bag and free whey is again allowed to drain. Relatively dry coagulum is then called chhana. It has on an average 50-55% moisture, 22-26% fat, 15-20% protein, 2.0-2.5% lactose and 1.8-2.2% ash. This is the base material for making Indian sweet like chumchum, chhana-murki, chhana kheer, rasagulla and sandesh (Bandhyopadhyay and Mathur, 1987).

Chhana making is principally a method of concentrating protein and fat of milk by the action of heat and acid. The removal of water soluble constituents (i.e. lactose, whey proteins and water soluble minerals) as whey which is inherent in such a process. A similar effect of concentrating protein and fat may be achieved by ultrafiltration, with an additional advantage of retaining whey proteins in the final product. Therefore an attempt has been made to make good quality chhana by the ultrafiltration technique. This was done because of two inherent advantages of such a methodology i) provides more yield of chhana per kg milk due to the recovery of whey protein in the product; ii) easy automation and process control.

2. PROCESS TECHNOLOGY

2.1 Raw milk:

Raw cow's milk was obtained from Research Centres' farm and was separated. Skim-milk so obtained was used for making ultrafiltered diafiltered retentate. Cream was concentrated by reseparation to make plastic cream of high fat content.

2.2 Making Ultrafiltered-Diafiltered Retentate (UDR):

The process of making UDR is shown in flow chart Fig.I. Skim-milk was heated to 95°C/5 min and cooled to 50°C before feeding to the ultrafiltration unit.
Skim-milk was concentrated to the concentration factor of 6.22 which is equivalent to 26.73% total solids (TS). The concentrate was diafiltered, with an equal amount of distilled water at 50°C in order to decrease lactose and to increase protein contents in dry matter of retentate. After diafiltration retentate had 23.57% total solids and 17.5% protein and 1.0% lactose. The retentate was stored at -35°C until used. Fresh plastic cream (66% fat and 70.34% TS) was added into the UDR for every batch of chhana, mixed for standardization of protein/fat ration as 0.722. The chhana mixture after proper standardization and mixing was having 36% TS, 13% protein and 18% fat. For every trial, 1 kg of such chhana mixture was taken to make actual chhana. The process flow chart is shown in Fig. 2.

![Process flow chart]

86 kg (TS = 9%)  
TS = 7.74 kg  
→ Skim milk  
↓  
Severe heating  
(95°C/5 min)  
↓  
Cooling to 50°C  
↓  
Ultrafiltration  
↓  
72.18 kg permeate  
(5.6% TS)  
TS = 4.04 kg

13.82 kg  
↓  
UF-retentate  
↓  
14.4 kg  
↓  
Addition of water at 50°C  
↓  
Diafiltration  
↓  
14.4 kg permeate  
(3.08% TS)  
TS = 0.443 kg

13.82 kg  
(TS = 23.57%)  
TS = 3.257 kg  
↓  
UF-diafiltered retentate  
↓  
Cooling to 10°C  
↓  
Stored at -35°C until used

Fig. 1. Process and Mass balance of UF-diafiltered retentate making

One kg of chhana mixture was taken and heated slowly to 60°C with slow stirring for proper mixing of UF-retentate and plastic cream. The temperature was then raised to 85-90°C and held for 5 min. Coagulant (1:5 diluted lactic acid) was added slowly at 75-80°C, so as to develop grains by acid coagulation. 1 kg of chhana mixture required 13-14 ml of above coagulant for desired grain formation. After grain
development, the contents were cooled to 50-60° C. At this temperature, the large grains were clearly visible. The coagulated mass was then taken in a dry clean muslin cloth and pressed with a 40 kg weight for 15-20 min. These were little expulsion of whey of high total solid contents. The dry mass after expulsion of free moisture was called chhana.

\[
\begin{align*}
0.733 \text{ Kg} & \rightarrow \text{UF-diafiltered retentate} \\
& \quad \text{(23.57\%)} \\
& \quad \downarrow \\
0.266 \text{ Kg} & \rightarrow \text{Addition of plastic cream} \\
& \quad \text{(66\% fat)} \\
& \quad \downarrow \\
0.999 \text{ Kg} & \quad \text{Chhana mixture} \\
& \quad \downarrow \\
& \quad \text{Heated slowly to 60°C for proper mixing} \\
& \quad \downarrow \\
& \quad \text{Heated to 85-90°C/5 min} \\
& \quad \downarrow \\
& \quad \text{Addition of coagulant (1.5 dil. lactic acid)} \\
& \quad \downarrow \\
& \quad \text{Cooling to 50-60°C} \\
& \quad \downarrow \\
0.74 \text{ Kg (43\%)} & \quad \text{Pressing} \\
& \quad \downarrow \\
\text{TS} = 0.318 \text{ Kg} & \Rightarrow \text{Chhana} \\
\end{align*}
\]

Fig. 2. Process and Mass balance of chhana making from UF-diafiltered retentate

2.3 Ultrafiltration Unit:

Ceramic filtration module (NO. P-1940) manufactured by Ceraver Co., France was used for ultrafiltration. The specifications of module are given in table 1. The ultrafiltration set-up was designed at this institute with a centrifugal pump of 5000 litres/hr capacity so as to obtain an average velocity of 5 m/sec. in the module. The set up of ultrafiltration unit is shown in Fig. 3. The operating conditions of ultrafiltration unit were: temp. = 50 ± 2° C, transmembrane pressure i.e. (pi + po) = 4 bars; where pi and po are inlet and outlet pressures of modules respectively. The ultrafiltration module was cleaned with a combination of water flushing, hot alkali (Ultrasil-25) at 75° C and acid detergent (Ultrasil-75) at 50° C, recirculation at inlet and outlet pressure of
4 and 2 bars respectively. The plant was said to be clean only when it regained the water flux in the range of 8000 - 5900 l/h m².

2.4. Sensory Evaluation:

The samples of chhana were judged by a panel of judges in comparison to the standard chhana made by the traditional method prescribed by De and Ray (1954). The sensory evaluation chart was having maximum scores as 35, 40 and 15 for flavour, body texture and appearance attributes. The overall acceptability was judged on a 9-point hedonic scale ranging from 9 (liked extremely) to 1 (disliked extremely).

2.5. Sampling and Analytical Methods:

Samples of chhana, whey and permeate were analysed for total solids, protein and lactose. Total solids were estimated by gravimetric method. Protein content was taken as 6.38 times nitrogen content determined by Kjeldahl analysis. Lactose content were determined by Technico-auto analyser.

3. PROCESS ECONOMICS

3.1 Average Flux During Ultrafiltration of Skim-Milk

The average flux started at a very high level of 114.45 l/h m² and slowly declined. The average flux to get concentration factor (CF) = 6.22 was 49.63 l/h m². The average protein retention coefficient of these membranes with severely heated skim milk was 0.99.

3.2 Mass Balance and Recovery of Total Solids (TS) in Chhana

3.2.1 Traditional Method: By this method, 100 kg of cow's milk (3.5% fat and 8.8% SNF) gave 84.57 kg of whey with 6.78% TS and 15.42 kg of chhana with 43% TS.

3.2.2 Ultrafiltration Method: By this method 100 kg of cow's milk (3.5% fat and 8.8% SNF) gave 18.3 kgs of chhana with 43% TS. The total solids recovery of the whole process was worked out to be 63.97%. The remaining 36.02% total solids were permeated out as permeate during pressing of processed chhana mixture. The total solids recovery by this process is 10% higher than the traditional method. The systematic calculations of mass balance are given in appendix II.

3.2.3 Extra yield of Chhana: Yield of chhana obtained from 100 kg of cow's milk (3.5% fat and 8.8% SNF) by traditional and ultrafiltration methods were 15.42 and 18.3 kg respectively. The percentage extra yield is calculated as

\[
\frac{18.3 - 15.42}{15.42} \times 100 = 18.68\%
\]

3.2.4. Saving in Milk: Kg of cow's whole milk (3.5% fat and 8.8% SNF) required for one kg chhana (43% TS) was as follows:

a) Traditional method \( \frac{100}{15.42} = 6.49\) kg
b) UF method \( \frac{100}{18.3} = 5.46 \text{ kg} \)

Therefore, saving of cow's milk per kg of chhana prepared was \((6.49 - 5.46) = 1.03 \text{ kg}\). And percentage saving is worked out to be

\[ \frac{1.03}{5.46} \times 100 = 6.68\% \]

It means 6.68% less cow milk would be required for making an equivalent amount of chhana by the new ultrafiltration method. The saving in milk or higher yield of chhana was mainly due to the recovery of whey proteins in chhana.

3.3 Sensory Quality of Chhana

The sensory score of traditional chhana and UF-chhana are shown in Table 2. Traditional chhana was taken as control and was given full scores. The UF chhana was scored in comparison to traditional chhana.

It is evident from the scores that there was no significant difference between the two types of chhana. Little difference was found in texture. The texture of UF-chhana was slightly less spongy as compared to the traditional chhana. UF-chhana was less coarser than traditional chhana. It was white in colour and was highly accepted by the judges.

4. CONCLUSION

It is possible to make good quality chhana from UF-retentate. The process of ultrafiltration gave 18.68% extra yield of chhana. This process is an industrially feasible process which provides 6.68% milk saving. The automation and easy process control is another advantage of this new process. This process has flexibility of operation. UF-diafiltered retentate can be made as per the availability of UF-plant and stored until used to make chhana. The reduction of bulk by making UF-retentate also reduces the transportation cost.

**Table 2: Sensory characteristics of traditional and UF-chhana**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Traditional chhana</th>
<th>UF-chhana</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flavour</td>
<td>35</td>
<td>33</td>
<td>UF-chhana was less acidic in flavour</td>
</tr>
<tr>
<td>Body and texture</td>
<td>40</td>
<td>37</td>
<td>UF chhana was less spongy and less coarser</td>
</tr>
<tr>
<td>Appearance</td>
<td>15</td>
<td>14</td>
<td>UF chhana had smooth and whitish appearance</td>
</tr>
<tr>
<td>Overall acceptability on 9 point hedone scale</td>
<td>8</td>
<td>7</td>
<td>liked</td>
</tr>
</tbody>
</table>

Higher product yield, easy automation and flexibility of operation are some of the main inherent advantages of this process.
For a country like India, where chhana and paneer are the main soft cheeses, this new ultrafiltration method has significant scope for adoption by the Indian dairy industry for large scale manufacture of chhana.

5. REFERENCES

Kundu, S. S. and De, S. 1972 Indian J. Dairy Sci., 25: 159-161

APPENDIX - I  Mass balance of chhana making by traditional method

100 kg cow's milk (3.5% fat, 8.8% SNF, 12.3% TS)
TS = 12.3 kg

↓

84.57 kg whey (6.7% TS)
TS = 5.67 kg
Heating and Coagulation

↓

15.42 kg chhana (43% TS)
TS = 6.63 kg
APPENDIX II

Mass balance of churma making by ultrafiltration method

100 kg cow's milk (12.3% TS) TS = 12.3 kg

↓

Separation

↓

94.7 kg skin-milk (9% TS)

↓

Ultrafiltration

↓

Addition of water

↓

Diafiltration

↓

15.21 kg UF-diafiltered retentate (TS = 23.57%)

↓

Addition of 5.21 kg cream

↓

20.72 kg churma mixture (TS = 36%)

↓

Heating or grain development, and pressing

↓

18.3 kg churma (TS = 43%)

TS = 7.869 kg

↓

5.30 kg cream (66% fat, 70.34% TS)

72.18 kg permeate (TS = 5.6%)

TS = 4.04 kg

14.4 kg permeate (3.08% TS)

TS = 0.448 kg

2.42 kg conc. whey (TS = 16.16%)

Total solid recovery = \( \frac{7.869}{12.3} \times 100 = 63.97\% \)
FIG. 3. FLOW DIAGRAM OF ULTRAFILTRATION UNIT WITH DEVICES FOR MEASURING PRESSURE FLOW RATE AND TEMPERATURE

1. FEED TANK
2. CIRCULATION PUMP
3. FEED VALVE
4. THERMOMETER
5. PRESSURE GAUGE
6. MEMBRANE MODULE
7. HEAT EXCHANGER
8. DEAERATING VALVE
9. BY-PASS VALVE
10. BLEED VALVE
11. PERMEATE

W - WATER
R - RETENTATE
APPLICATION OF MEMBRANE TECHNOLOGY IN FRUIT AND VEGETABLE JUICE INDUSTRY

Mr. D.K. Sharma
Dairy Technology Division, NDRI (ICAR), Karnal 132 001

1. INTRODUCTION

Reverse osmosis (RO) and ultrafiltration (UF) are now used extensively in food and dairy industries with the introduction of new composite membranes and tubular systems.

RO is a single phase concentration process which uses a pressure gradient across a semi-permeable membrane to squeeze water through membrane, retaining most compounds including low molecular weight organics and salts. Since, there is no phase change, the R.O. process of concentration is extremely energy efficient, compared to both evaporation and freeze concentration. RO can operate over a wide temperature range from 5 to 80°C. Low temperature RO is an effective process to avoid heat spoilage of some products such as fruit juices.

Ultrafiltration is a related process but uses much lower pressure, typically 1 to 10 bars, and much more open membranes which pass salts, sugar organics in the molecular weight range typically from 5000 to 100,000 depending on the membrane type. It is not limited by osmotic pressures since the sugars are not concentrated. Both RO and UF are being used in fruit and vegetable juice industry as a unit operation for concentration or aroma recovery and clarification of juices, respectively.

2. FRUIT JUICE CONCENTRATION AND CLARIFICATION

Traditional methods of fruit juice production involve several batch operations which are labor and time consuming. In a typical traditional setup, after preliminary sorting/handling/washing, peeling steps, depending on the fruit, the fruit is crushed and sent through presses and screens to remove the large particulates. If a clear juice is to be produced, the press juice is pasteurized, then treated with an enzyme (pectinase) to hydrolyze the pectin and reduce the cloudiness. The enzyme treatment also make the subsequent filtration easier presumably by lowering the juice viscosity. The preliminary clarification, where a fining agent such as gelatine is added and juice held for 20-40 hours, after decanting, the juice goes for precoat filtration, using diatomaceous earth as a filter aids. (Refer schematic-1)

The primary goal of UF in fruit industry is to replace the holding, filtration and decantation steps of traditional process. Moreover, very small quantity of enzyme (pectinase) to the order of one-third to one-fourth of quantity used in traditional process, is required while clarifying the juice with UF-process. Enzyme treatment in
this case is required only to reduce viscosity of juice by partially hydrolysing the pectin mainly to improve the performance of UF-unit by evident increase in flux rate.

3. JUICE CLARIFICATION USING UF-PROCESS

Membrane: The clarification process essentially a process to remove pectin, enzyme and other fibrous micromolecules from sugars and flavour components, constituting the clear juice. To separate these molecules a semipermeable membrane made of a polysulphone in cut-off range of 20,000-25,000 is required. The temperature of UF may be high (50-55°C) or low (10-15°C) depending on the type of juice and thermal sensitivity.

Module: It is advisable to use tubular modules through the viscous partially depectinized juice can go directly to the UF-systems. If thin-channel or hollow fiber equipment is used, some pre-filtration is necessary, usually with 80-mesh screen.

Typically pressures of 3-20 bars are used in UF-clarification process.

System: Since fruit juices have very low level of retained solids the optimum mode of operation is the batch operation with partial recycle of retentate, i.e. where the bulk of the retentate is within the recycle loop, and a small portion is used to 'top off' the feed tank. This should offer considerable savings over multi-stage recycle systems. Further savings in capital cost and reduction in hold up volume can achieved by judicious arrangement of modules in series and in parallel.

A pectinase treated juice gives permeability (flux) in the range of 120-130 litres/m²/hr.

Rententate and Permeate

In the process of manufacturing clear single-strength juice by UF, the permeate (sugars and flavour components minerals, water, vitamins) is the desired product stream. The ultrafiltered permeate the product, of this process is eventually sterile and if handled carefully and in an aseptic manner, should not require a subsequent treatment prior to storage or bottling.

Apple Juice UF

The UF process produces a high quality, clear from de-pectinised apple juice feed in a single step.

The capital costs of equipment and the hold-up volume of apple juice in conventional sedimentation centrifuge, filter press (with filter aids) and final filter press sequence is reduced to a rapid single step process.

Each producer has different operating techniques and costs, but the ultrafiltration process generates cost savings and man-power reduction in:

i) The quantity of enzymes required to depectinise the apple juice.

ii) Filter aids, bentonite, and filtration step.

iii) Improved overall extraction efficiency typically 97% against 90-93% typical for traditional process.
iv) No holding for 20-30 hours for fineing process, the bottling can be carried out 2 hours after start-up.

Lime Juice UF

Lime juice is usually clarified on a single stage, batch UF process. This process illustrates the potential for UF Process, to recover a valuable secondary product in this case, the lime juice essential oil fraction, by a low temperature, non-heat degrading process. The recovery of clear juice is typically in the range 88-95%.

The other fruit like cranberry, pear and grape juice are also being clarified using UF process.

4. JUICE CONCENTRATION USING RO

Reverse osmosis occurs when pressure greater than the osmosis pressure is exerted on a solution in contact with a semi-permeable membrane. Water flows through the membrane and the solution retained by the membrane is concentrated.

The process occurs in the liquid phase at ambient or higher temperature and uses energy more efficiently than processes which involve a change of phase.

The advantages in concentrating fruit juices using a low cost, energy efficient process combined with minimum heat damage to colour, aroma and viscosity characteristics of juice, were first noted in work on orange and apple juice by Merson and Morgan (1968) and on grapefruit, apple and orange juice by Gheradi, et al. (1972).

Membrane: Cellulose acetate membranes used in concentration of orange juice retained oil-soluble aromas, but still higher membranes are required to retain the water soluble esters, alcohols, aldehydes and acids.

Retention of water soluble aroma compounds have been possible with ZF 99 (PCI Ltd.) in tubular form with combination of high fluxes and chemical, physical stability of membranes.

Modules: Tubular configuration is highly suitable for fruit and vegetable juice concentration. It permits operation at uniform high solution flow velocities to minimise fouling and allow cleaning-in-place. Tubular modules can concentrate raw as well as clear juices which perhaps not possible with hollow fiber or plate and frame system. The typical operating pressures of 40-70 bars are required in concentration of fruit juices upto 8.5° Brix.

Advantages:

Reverse osmosis is essentially used as a energy saving device for preconcentrating of fruit juice upto 8.5° Brix. It has following advantages:

- Uses only electrical energy to raise the pressure of juice feed.
- Total operating costs are typically 5 to 10 times lower than normal evaporators.
- Process control is simple and product Brix level is automatically controlled.
- No cooling water equipment needed.
- Passto (Tomato paste) type products (6-8.5 Brix) made by RO has better flavour, color and better nutritive value.

5. TYPICAL INDUSTRIAL APPLICATIONS

5.1. Tomato Juice Concentration by RO

Currently there are a number of installations in operation in Italy, Spain and France, concentrating juice 8 to 9% NTSS, using RO process. The RO concentrate (6-8.5 Brix) packaged, as a product called "Passato" or 'Belle Tomate'.

The Passato product for tomato sauces such as bolognaise, Chilli or pizza, as well as soups and drinks. It has been observed that Passato produced by reverse osmosis has a redder colour since browning is minimised; It has a higher viscosity for given solids content, and the flavour is closer to fresh tomatoes. Passato was only known in Italy, but now it is a product that is gaining popularity in Europe and may well eventually replace canned tomatoes for culinary purposes.

Case Study: In 1984, one large RO tomato concentration plant was installed by PCI, England in Coper, Ravarino, Italy for production of 'Passato'. The plant was capable of producing continuously an 8.5° Brix product from a 37.5 or 25 m³/hr feed tomato juice (4.5-5° Brix). The RO product is pasteurized and either bottled as 'Passato' product or stored in sterile storage tanks. In this 4 stage RO plant, the operating costs include about 175 KW electrical power and membrane replacement cost, to give a total operating cost of £1.15-1.30/m³ water removed. The existing evaporator had an operating cost (steam plus electrical power) of £7.25 per m³ of water removed.

At maximum capacity, the RO plant removes 17.65 m³/hr of water, with a calculated saving in a 50 day season of over £120,000.

The technical advantages of RO product as an 8-8.5° Brix passato product, compared to the original product produced by evaporation have been:

- Improved color compared to evaporator product.
- No loss of sugars, salts and important flavour components, amino acids etc. are retained by RO system which improves flavour and recovery of product.
- Increased viscosity (10-25%) because of decreased heat damage.

In another processing plant in Italy, the three stage PCI RO plant has total capacity of 126 m³/hr of 4.5° Brix. Tomato juice feed. Upto 59.3m³/hr of water is removed in pre-concentrating to 8.5° Brix. The two evaporators then remove the final 47.1m³/hr of water to produce 28-30° Brix product. The total saving of 50 days processing using RO. In preconcentration was calculated as £ 400,000. In economic terms the project has a calculated payback of less than three years.
5.2 Orange Juice RO:

It has been confirmed by independent expert taste panels that the 20° Brix RO product re-diluted to 11-12° Brix feed strength retains all natural orange juice characteristics of taste and flavour.

The RO process provides the preconcentrated orange juice at 14 to 18° Brix into an evaporator.

In addition to the advantages of low cost pre-concentration, economic savings and factory capacity expansion, the low cost RO pre-concentrate at 17-20° Brix can be concentrated to 40-65° Brix by flash evaporation to produce very high quality concentrate. The effective capacity of the flash evaporator is increased and the very high steam usage (typical efficiency is 1.1 Kg. steam per Kg. water evaporated) may be reduced to between 40-60% of the existing cost for the same production rate. In order to reduce heat degradation to a minimum, orange juice RO is carried out typically between 20-30° C.

5.3. Apple Juice RO

Apple juice can be concentrated using PCI tubular module at 30-50° C. The depectinated apple juice (clear juice) can be economically concentrated to 20-25° Brix. The retention of sugar & flavouring components such as Ethyl-2-methyl butyrate, malic acid, citric acid, calcium, Potassium, Fructose, Glucose was in the range of 95 to 99%. The Retention of low molecular weight organic compounds by new ZF 99 (PCI Ltd) membrane are illustrated in fig.-2 (Pepper et al, 1985). According to an estimate a RO plant which concentrate 8000 litres/hr of apple juice from 10° to 20° Brix has following cost figures:

Capital cost= £ 190,000
Operating Costs (assuming 2000 hours per season
(a) Membrane (over 3 seasons) : £ 8,700
(b) Electricity (40 KW at £ 0.04/KWh) :£ 3,700
(c) CleaningChemicals £ 1,000
Total £ 12,700/per year
Cost of water removal= £ 1.34/m³

5.4. Beet Juice RO

It is now possible to concentrate raw beet juice, thin beet juice and steffens filtrate (diluted molasses with 3.5% solids) using tubular polysulphone RO membranes at 60-70° C from 15° Brix to 30° Brix. Typically optimum pressure for RO of beet juice is 55-60 bars at 60° C, with 30-35 Kg/m²/hr. The velocity of flux is kept at 2m/sec.

It is quite easy to perform RO on thin beet juice upto 30° Brix with two stage RO recirculation system. However, raw juice with substantial amount of fibre, grit and clay, damaged the piston pump suction valves and the mechanical seals on the recirculation pumps. For this reason raw juice has been pre-filtered through course 650 micron bag filter. It has been observed that fluxes during concentration do not
deteriorate significantly over runs up to 20 hours duration. The most likely sources of fouling has been the calcium salts.

The polysulphone membranes after beet juice RO concentration are cleaned satisfactorily with little change in initial water flux with following cleaning cycle:

a) 0.3% by weight nitric acid at 40-50°C for 30 min.
b) rinse with water at 50°C for 10 min.
c) 0.25% NaoH at 40-50°C for 30 min.
d) rinse with water at 50°C in 10 mins.
e) Sterilization with 500 ppm H₂O₂.

5.5. Economics of Beet Juice RO

The figures are based on typical plant with the capacity to treat 200 m³/hr. of thin juice and concentration from 14° Brix to 26° Brix. Operating and running costs are based on running the plant 24 hours a day for 20 days and removing 93 m³/hr. of water.
Capital Cost : £ 250,000 to £ 1,750,000.

5.6. Main Operating Costs

a) Membrane replacement cost (after 6000 hrs.)= £ 0.36/m³/WR
b) Power 600 KW/hr.
     Total  = £ 0.59/m³/water removed

In equivalent energy terms RO requires less than one-tenth the energy of 6-effect evaporators.

6. CONCLUSION

In recent years, Ultrafiltration has become an economically viable alternative for clarification of wide variety of fruit juice in comparison to conventional method of clarification. Both technology and membrane system are now available in international market from Europe, USA, Japan etc. There are few Indian manufacturers providing tubulars and spiral-wound modules which are worth trying for fruit juice concentration.

Reverse osmosis is well established process now for concentration or preconcentration of raw and clear depectinated juice from fruits and vegetables. It is established beyond doubts that this process consumes 10 times less energy for removing water when compared with conventional evaporators, with however, limitation of concentration levels. Technologies are standardized now for concentration of tomato juice, orange juice, apple juice and beet juice.

7. REFERENCES

Pepper, D., Orchard, A.C.J.(1985) Concentration of Tomato juice and other fruit and fruit juices by reverse osmosis, Desalination, 53, 157-166.
APPLE JUICE CLARIFICATION

TRADITIONAL PROCESS

Juice from press outlet

Flash pasteurization 110°C-55°C

Enzyme Treatment

Enzyme Treatment

55°C - 2h

Cooling

Bentonite Gelatine

Fining Settling

Clear Juice

Precipitate

Concentration

Centrifugal Separator

Clear Juice

Sludge

Distemite earth filtration

Floc filtration

Pasteurization

Concentration

Bottling

ULTRAFILTRATION PROCESS

Juice from press outlet

Flash pasteurization 110°C-55°C

Enzyme Treatment

Process batch from feed tank

Bottling

Concentration

Schematic-1
MANUFACTURE OF WHEY PROTEIN CONCENTRATE
BY ULTRAFILTRATION PROCESS

Dr. R.S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Ultrafiltration process is being widely adopted in the dairy industry especially for the concentration and fractionation of whey and milk. Now this has become a well established technology for the recovery of proteins. However, the permeation behaviour and the characteristic of whey protein concentrate obtained by ultrafiltration, widely vary with the type of feed stream, pH, ionic strength and various other constitutional make up of the system (Moubossis, 1980; Cheryan, 1986; Daufin and Merin, 1992; Maubois, 1980; Jayaprakasha et al, 1995). The economy of the process and the characteristics of the resultant whey protein concentrate (WPC) dependent on the permeation behaviour of the constituents during ultrafiltration.

2. WHEY PROCESSING BY ULTRAFILTRATION

The principal aim of ultrafiltering whey is to concentrate the native whey proteins in order to obtain a whey protein powder with varying protein contents. If, for example, a 35% protein powder is wanted, sweet whey with 6% total solids is ultrafiltered up to a dry matter content of 10.0%; the nitrogen substances consist of 3.2% protein and 0.3% NPN. By subsequent evaporation and spray drying (up to 96% dry matter) a 35% protein powder is obtained. The maximum dry matter content of the retentate is about 25% which permits a protein content of 60-65% in the powdered product. When whey is concentrated about 20 times by UF a dry matter content of 18-20% is attainable (Renner and El-Salam, 1991).

At a protein level of 34% of total solids, WPC has an approximate composition equal to non-fat dry milk; differences lie in the mineral profile of the ash content and in the type of proteins.

In order to achieve higher protein values (upto 90% of dry matter), one or more diafiltration steps may follow. Diafiltration means that water is added to the retentate, thereby the viscosity is reduced, and the concentration of lactose, ash, and NPN is decreased by further UF (Zall, 1982; Vuillemand et al., 1989). A process scheme for the UF of whey is given including the resulting quantities of retentate, permeate and powdered product. The spray drying process for this product is conventional.

How to increase the flux of whey?

A. A number of whey pretreatments have been developed to improve UF membrane flux rate for fractionating whey proteins and for improving the functional properties of WPC (Kuo and Cheryan, 1984; Cheryan, 1986; Jayaprakasha et al, 1994).
B. Whey must be filtered or centrifuged to remove suspended cheese or casein particles and to remove fat.

C. A method which provides complete removal of lipoproteins, lipids, and colloidal calcium phosphate is based on cooling cheese whey to 0-5°C, adding calcium chloride, adjusting to pH 7.3, warming to 50°C, and removing the insoluble precipitate that is formed by centrifugation or decantation; UF permeation flux rate of pretreated whey was about double that for control whey; pretreated whey was essentially turbidity-free, contained 85% less milk fat, 37% more calcium and 40% less phosphorus than whey.

D. Cottage cheese whey was treated to minimize effects of calcium on membrane fouling during UF by stepwise pH adjustment from 4.5 to 1.5; chelation of calcium with EDTA (disodium ethylenediamine tetraacetic acid) or citric acid; calcium chelation followed by pH adjustment to 2.5; and calcium replacement with sodium by ion exchange. All treatments resulting in elimination of free calcium improved the flux. Highest flux increase (53%) in the 8-h-processing was for citric acid after pH adjustment to 2.5, calcium replacement by ion exchange improved the flux when ultrafiltering acid whey.
E. UF permeation rates were greater with higher UF temperatures and with preheating the whey for 30-40 min at temperatures (68-72°C) higher than the UF temperature (50°C) (Gupta and Renter, 1987).

Cleaning and sanitization of the ultrafiltration plant are of major importance to the economics of WPC manufacture because failure to achieve a satisfactory standard may result in a reduction in flux, time of operation on product and membrane life, and the production of WPC having unsatisfactory microbiological quality. The procedures employed are generally specific to both the type of plant and the type of product being manufactured. A typical sequence would involve (Patel et al., 1990):

1. a thorough rinse with clean water to remove residual retentate and permeate;
2. an alkaline detergent wash (which may include proteolytic and lipolytic enzymes);
3. a clean water rinse;
4. a rinse with dilute Nitric acid solution;
5. a clean water rinse;
6. a rinse with sanitizing solution (e.g. dilute hydrogen peroxide); a clean water rinse.

Clean water flux is commonly used to indicate the effectiveness of the cleaning process. If the flux is insufficient, the procedure or parts of it may be repeated until a satisfactory water flux is achieved.

3. PROCESS OPTIMIZATION FOR THE PRODUCTION OF WHEY PROTEIN CONCENTRATE FROM BUFFALO MILK

3.1. Cheddar cheese whey

The flux rate as affected by temperature of operation pH and heat treatments of whey was studied. Retention of various constituents during ultrafiltration and the effect UF & DF on the composition of the retentate was also studied.

3.2. Temperature of operation

Clarified and pasteurized buffalo whey was concentrated by UF at 40° and 50°C. It was observed that there is a significant difference in the flux obtained at 40° and 50°C. When the temperature was raised from 40 to 50°C, there was significant increase in the flux. The initial flux was observed to be 35.07 and 54.80 1/m/hr, respectively at 40° and 50°C. Whereas the average flux values appeared to be 23.79 and 34.00 L/m/hr, respectively at the above temperature. Significant improvement of flux at higher temperature of operation could be ascribed to decrease in viscosity of the fluid as well as increase in diffusivity of protein increased to an average rate of 3 to 3.5 per cent per °C rise in temperature. Hence, it is beneficial to operate UF at 50°C.
3.3. Effect of pH and heat treatment

The effect of various pH adjustments and pre-heating of whey on the resultant flux has been studied. When the clarified BW was subjected to 60°C/30 min heating at various pH levels, the flux rate appeared to be better at extreme pH values. At pH 3.0 and 7.2, flux was significantly higher than at any other pH levels. The initial flux at pH 3.0, 4.5, 5.6, 6.4 and 7.2 was estimated to be 60.60, 49.60, 53.60, 55.50 and 62.30 1/m h respectively. Whereas the respective average flux values for 95% volume reduction were 44.29, 20.89, 28.75, 34.36 and 46.88 1/h/m. Similarly when the whey was heated to 80°C/15 sec, the flux rate was better, compared to 60°C/30 min heating at all levels of pH. The initial flux values were found to be 62.40, 51.70, 55.60, 57.40 and 64.20 1/m h. Whereas the mean flux values at the above pH values for 95% volume reduction were 48.44, 22.77, 30.50, 36.29 and 51.71 1/m h (Jayaprakasha, 1992).

It is evident that, as the volume reduction increased, the flux decreased irrespective of the treatment imparted to the whey. This decrease in flux can be attributed to the added resistance from fouling and concentration polarization of the membrane surface and its pores as a result of protein and salt deposition. However, the rate of decline in flux varied significantly with the pH and heat treatment of whey. This can be ascribed to the fact that UF performance is strongly dependent on physico-chemical characteristics (complexation of calcium ions, & pH change) which refers to the solute interaction and solute membrane interactions. The intensity of these interactions varies with the kind of pretreatment imparted to whey. Hence, the flux varied widely with the treatments. The change in pH and heat treatments affect the status of calcium salts and the configuration of protein and hence the flux.

When BW was processed at 7.2 pH or pH 3.0, the flux rate was observed to be higher than at normal pH (6.4). At pH 4.5, the net charge on the proteins is low and hence dispersion of protein is poor. They get adsorbed on the surface of the membrane, forming gel layer which results in the lowest flux rate. As the pH is lowered from 4.5, the dispersion of proteins improves calcium gets solubilized and pass through the membrane without much fouling, thus increasing the flux rate significantly.

At pH 5.6 for example, the flux improved but still is at a lower side, probably because of certain deposition of calcium phosphate as amorphous tricalcium phosphate and adsorption of beta lactoglobulin, as the pH is near to its isoelectric point. It is surprising to note a drastic increase in the flux at pH 7.2. This pronounced increase in the permeate flux may be due to heating of whey at elevated pH. Under such conditions, a considerable precipitation of calcium phosphate is expected in such a form (probably as hydroxy apatite) that results in reduced fouling of membrane. Hayes et al. (1974) observed that addition of calcium to whey and adjusting pH above 6.5 and heating, increased the flux. As the calcium content of BW is higher, heating at 7.2 pH probably resulted in calcium induced protein interaction, which aided in larger aggregate or apatite formation, which were found to be nonfouling. Heating whey to a temperature of 80°C/15 sec resulted in better flux than at 60°C/30 min. Probably higher temperature is needed for the apatite formation or for the calcium induced beta lactoglobulin self aggregation or for the protein-protein interactions. Muller and Harper
(1979) also observed an increase in flux by 50% when cheese whey was heated to 80°C/15 sec instead of pasteurization temperature.

3.4. Compositional changes during Ultrafiltration

Preliminary trials have shown that it is possible to obtain a maximum of 26.5% solids (97.5% volume reduction) by concentrating BW through UF. However, due to low flux rate caused by high viscosity, the concentration was restricted to 95% volume reduction (21.60% TS).

The changes occurring during concentration with respect to protein, lactose, ash, NPN, calcium and phosphorus were estimated at a regular interval of volume reduction (Fig. 1 and 2). The protein content of retentate on DM basis at 0, 30, 50, 70, 80, 90, 95% volume reduction was 14.98, 20.61, 23.67, 25.90, 36.72, 47.61 and 63.79% respectively. Thus it is possible to obtain desired levels of protein in the end product depending on the degree of volume reduction. For example by 80% volume reduction, retentate possess protein content (on DM basis) equivalent to that of skim milk powder. The changes with respect to lactose were quite opposite to that of changes in protein. The lactose content of the retentate on DM basis decreased in the order of 76.13, 66.91, 62.38, 58.36, 54.99, 41.10 and 27.54% after 95% volume reduction. From the results it is clear that varying degree of lactose can be obtained in whey protein concentrates by monitoring volume reduction. At 0, 30, 50, 70, 80, 90 and 95% volume reduction, the respective ash content of the retentate was 8.20, 8.14, 8.40, 8.66, 8.28, 7.13 and 67.23% (on DM basis).

The calcium, phosphorus and NPN contents gradually increased up to a level of 10% volume reduction which declined thereafter (on DM basis) to a great extent. The respective NPN content at 0, 30, 50, 70, 80 and 95% volume reduction (on DM basis) was found to be 0.72, 0.70, 0.69, 0.72, 0.71, 0.53 and 0.36%. Similarly the respective calcium and phosphorus content at the above level of volume reduction were found to be 0.79 and 0.67, 1.0 and 0.77, 1.27 and 0.87, 1.41 and 0.94, 1.40 and 0.91, 1.07 and 0.689 and 0.76 and 0.47%.

The compositional changes during ultrafiltration of BW have followed the similar pattern as reported by other workers for cow milk cheese whey. Marshal and Harper (1988) have observed increase of protein content from 12 to 66% (on DM basis) decrease in lactose content from 79 to 28%, a smaller reduction in ash content from 9 to 6% during UF of cheese whey. In our experiments with BW increase of protein content from 14.98 to 63.79, decrease in lactose and ash contents from 76.13 to 27.54 and 8.20 to 6.23% were observed, respectively. These changes with respect to protein, lactose and ash are also in agreement with the findings of Cheryan (1986) and Gupta and Reuter (1987). It was observed that, during UF of BW, at the volume reduction progressed, the protein content increased and lactose and ash content decreased. The increase in protein content was found to be very slow at the beginning stages of volume reduction and later on there was rapid increase in protein content. Whereas rate of decrease of lactose was slow at the beginning and was rapid at later stages of concentration. Similarly, the ash content slightly increased at the initial stages of volume reduction whereas it decreased later.
FIG 1. COMPOSITIONAL CHANGES DURING ULTRAFILTRATION OF BUFFALO MILK CHEESE WHEY

- Ash
- Protein
- Lactose

Content on dry matter basis (per cent)

Volume reduction [per cent]
BUFFALO MILK CHEESE WHEY
ULTRAFILTRATION AND DIAFILTRATION OF
COMPOSITIONAL CHANGES DURING

FIG. 2
It is possible to obtain product having varying degree of protein/TS ratio by controlling the volume reduction. Higher the volume reduction, greater is the protein to TS ratio, in our experiments the protein content at 95% volume reduction was found to be 13.65 for a TS content of 21.60.

Results also indicated that the increase in volume reduction resulted in decrease of NPN compounds as these low molecular weight compounds permeable through UF membranes. The ratio of NPN to true protein decreased as the concentration factor increased.

Similarly, Calcium and Phosphorus content on DM basis increased with the increase in concentration until a certain degree of volume reduction, thereafter a decreasing trend was observed. This can be ascribed to the fact that as the solubility of calcium and phosphorus is low, higher proportion of them would be retained. However, as the UF progress, there will be a build up of internal pressure which aids in driving out more and more of calcium and phosphorus along with the permeate. Hence, at later stages of volume reduction the retention was minimal. These results are in confirmation with the observations of other workers.

3.5. Compositional changes by diafiltration

By UF of BW to 95% volume reduction, the protein content of retentate (on DM basis) increased to 63.75% from an initial value of 14.89%. It increased further to 79.98% after first stage of DF and to 85.92% after second stage DF. Similarly, the content of other components at the end of UF, first stage DF and second stage DF respectively were 27.31, 11.2 and 4.6% for lactose, 6.23, 3.44 and 2.85 for ash and 2.67, 5.47 and 6.83% for fat. Whereas the corresponding percentages of calcium and phosphorus content in the total ash, were 12.02, 22.09 and 26.3% and 7.5, 13.08 and 15.43%.

These results indicate that it is possible to attain as high as 85.95% protein by UF of BW followed by two stages DF. The lactose content reduced to as low as 4.60% and ash to 2.85%. The increase in protein and decrease in lactose, ash and NPN content during UF and DF could be attributed to the addition of water to the UF retentate, which aids in reducing the viscosity and, thereby more of lactose, minerals and low molecular weight nitrogenous compounds pass along with permeate. During DF process it was observed that retention of calcium and phosphorus was high whereas total ash retention decreased to a great extent. This could be ascribed to the fact that, repeated DF of whey results in removal of potassium, sodium, and magnesium to a greater extent and phosphorus to a lesser extent. Retention of calcium was found to be high during DF of BW.

3.6. Manufacture of spray dried whey protein concentrates

As shown by the results, it is possible to attain differential degree of composition and protein content in WPC depending on the requirement by controlling the degree of concentration or the volume reduction. Manufacture of WPC involves UF of whey to a required degree of concentration followed by vacuum evaporation and drying or directly spray drying after UF concentration of whey.
Six hundred litres of clarified buffalo milk cheddar cheese whey was adjusted to pH of 7.2 and subjected to a heat treatment of 80 °C/15 sec and cooled to 50°C. UF of pretreated buffalo whey was carried out at a temperature of 50°C to a level of 85% volume reduction. The retentate so obtained was directly spray dried at 180°C inlet and 80°C outlet temperature with a atomizer speed of 25000 rpm by using Anhydro-Denmark (35 kg evaporation components) spray drier. Spray dried WPC was cooled to room temperature packed in polyethylene and metallized polyester packaging materials.

4. CHEMICAL COMPOSITION OF DRIED WHEY PROTEIN CONCENTRATE

Spray dried WPC prepared from BW (WPC 45) and commercial whey protein concentrate (WPC 26, 70 and 80) were analysed for their chemical composition (Fig. 3).

4.1. Chemical composition

The major components such as moisture, protein, fat, lactose and ash contents of the samples were analysed. It was observed that various components varied with the protein content of the samples. The samples WPC 26, WPC 45, WPC 70 and WPC 80 had protein content of 25.11, 43.46, 71.16 and 80.60 per cent. The lactose content of these samples was 53.64, 42.76, 14.37 and 4.45%, respectively. Similarly, in contrast to lactose, the fat contents of these products were found to increase as the protein content increased. The respective fat content of WPC 26, WPC 45, WPC 70 and WPC 80 was, 1.42, 4.45, 6.70 and 7.17%. Slight variation in the moisture content of the dried WPCs was observed. The samples WPC 26, WPC 45, WPC 70 and WPC 80 had moisture content of 4.80, 3.74, 4.41 and 3.62 %, respectively. Wide variation in the ash content of the above samples was observed. The respective ash content of the above samples was found to be 15.03, 5.58, 3.36 and 4.01%.

Slight variation in the moisture content of dried WPCs could be ascribed to the variation in spray drying temperature, type of spray dried employed, variation in the degree of concentration of UF retentate used for spray drying. However, all the samples observed to contain moisture below 5%. The protein, fat and lactose contents are inter dependent. It was observed that higher the protein content, higher was the fat content, since the fat, being impermeable, also gets concentrated during the operation similar reports are reported by earlier workers. As the protein content in retentate increased, lactose which is lost through permeate increased. The commercial product WPC 80 having 80.60% protein contained as low as 4.45% lactose. Generally, it is presumed that as the protein content increases or the higher the volume reduction lower should be the ash content. However, WPC 70 had shown lower ash content (3.36%) than the WPC 80 (4.16%). Probably, during WPC 70 production, the UF might have been carried out at low pH values as shown by a low pH of 3.2 as against pH 6.3 for WPC powder. It has been removal of more minerals through permeate thus considerably decreasing the ash content of WPCs. Ash content of WPCs also depends on the initial load of minerals in whey, preheat treatment imparted, pH, type of whey and thge neutralizers used. Hence, wide variations in the ash contents were observed.
4.2. Minerals profile of whey protein concentrate

Whey protein concentrates were analysed for their mineral profile. The presence of minerals such as calcium, phosphorus, potassium, magnesium and sodium are investigated.

It was estimated that WPC 26 had 1062, 1273, 4588, 1501 and 226 mg/100g, calcium, phosphorus, potassium, sodium and magnesium, whereas WPC 45 was found to contain 715, 504, 965, 332 and 98 mg/100g WPC 70, 250, 34.74, 190, 63.75 and 27.15 mg/100g of calcium, phosphorus, potassium, sodium and magnesium respectively. The WPC 26 had all the minerals in higher proportion which is also reflected by higher ash content of the sample this is probably due to addition of neutralizers to whey and also the addition of potassium nitrate during cheese preparation which might have resulted in higher amount of potassium in whey. As the level of protein increased the content of various minerals decreased, possibly due to permeation of more and more minerals with progressive concentration of whey by UF. The rate of the intensity of permeation of minerals was found to be higher of higher degree of concentration. The amount of other minerals were found to be very less in WPC 80 as compared to other samples.

5. ABSTRACT

Buffalo milk cheddar cheese whey was fractionated by employing Hollow fiber ultrafiltration plant. Whey preheated to 80°C/15 sec at pH 7.2 and processed at 50°C resulted in maximum flux. A maximum volume reduction of 97.5 per cent was attained, which resulted in 26.60% total solids in the retentate. However, for economical concentration, it was found necessary to restrict the volume reduction to a level of 95% (21.60% TS). At this concentration the retentate had 63.79% protein, 27.54% lactose, 6.23% ash. To attain higher levels of protein in the retentate two stage diafiltration was followed. By first stage diafiltration, as high as 80% protein was attained (on DM basis) whereas by second stage diafiltration 85% protein (on DM basis) was attained. The ultrafiltered whey was also spray dried and the resultant WPC had 3.74, 43.46, 42.46, 5.58 and 4.45% moisture, protein, lactose, ash and fat respectively. Commercial WPCs such as WPC 26, WPC 70, and WPC 80 had 4.8, 4.41 and 3.62% moisture, 25.11, 71.16 and 80.60% protein, 53.64, 14.37 and 4.45% lactose, 15.03, 3.36 and 4.46% ash, and 1.42, 6.7 and 7.17% fat respectively.

6. REFERENCES


MECHANIZATION OF PANEER MANUFACTURE EMPLOYING ULTRAFILTRATION

DR. K. V. S. S. Rao
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Paneer is a traditional heat-acid coagulated milk product and it is very popular in the North-western parts of India and the Southern regions of Jammu and Kashmir. Typically paneer is white in appearance with spongy body, close knit texture, possessing sweetish-acidic nutty flavour (Verma and Mathur, 1987; Bandyopadhyay and Mathur, 1987). In the absence of reliable statistics, it is believed that about 5 percent of the total milk produced in India is converted into paneer (Rao et al., 1991). The product technology and quality show wide variations as it is mainly produced on cottage scale. Paneer is mostly used for preparing culinary dishes and snacks. It contains approximately 50-55 percent moisture, 23-26 percent fat, 17-18 percent protein, 2-2.5 percent lactose and 1.5-2 percent minerals (Singh et al., 1984; Sachdeva and Singh, 1995; Singh and Kanawjia, 1988). Paneer manufacture essentially involves heat/acid coagulation of standardized milk followed by pressing of the coagulum. The existing batch manufacturing technique is labour and energy intensive and is susceptible to environmental contamination. Manual handling at various stages of processing lead to microbial spoilage which is a serious limiting factor for an organized nationwide marketing. Furthermore, lack of effective packaging system limits its life to only one day or two at room temperature. In recent years, following a boom in the production and consumption of paneer there has been a thrust on upgrading the existing technologies.

2. STATUS OF EXISTING TECHNOLOGY

Spurred by the large demand for paneer, particularly in the metropolitan cities, attempts have been made to upgrade the traditional process. Noteworthy achievements have been made to utilize the available cheese/casein manufacturing equipment. This approach permits handling of 1,000-5,000 litres of milk per batch. Shelf life upto a maximum of 3-4 weeks under refrigeration conditions through the application of antimicrobial/antifungal agents has been achieved on pilot scale operations. Notwithstanding these developments, the existing technological approach based on the traditional manufacturing technique of coagulating milk by acid/heat resulting in whey separation suffers from the following limitations:

i. Wastage of nearly half of milk solids in the form of whey leading to uneconomical utilization of precious milk nutrients and consequent environmental pollution.
ii. Variation in quality from batch-to-batch.
iii. Lack of 'in-process' quality control  
iv. Inability to avail the opportunities for consolidating the advantage of bactericidal effect of heat/acid coagulation to extend shelf life.  
v. Lack of opportunities for through-and-through mechanized manufacturing and packaging operations  
vi. Limitation of scope for employing newer concepts of energy conservation mainly thermal energy, from hot whey after completion of coagulation process  
vii. With the use of cheese/casein vats, the upper limit for refinement of paneer making by batch operations seems to have been attained and further attempts for process upgrading with this approach would not yield far reaching results.

It is, therefore, apparent that overcoming various process limitations in the existing technology, a differential conceptual approach breaking away from traditional technology in terms of both processes and equipments would be sine qua non for meeting the technological requirements of the industry.

3. ULTRAFILTRATION - A FEASIBLE ALTERNATIVE

Membrane processes such as Ultrafiltration facilitates separation of lactose and soluble salts along with water from milk, thus concentrating proteins (including whey proteins) and fat of milk in the retentate (Patel et al., 1986). If UF retentate can be converted into paneer, it can eliminate the loss of about 0.5 percent whey proteins which otherwise result in traditional process. Thus by employing UF technology, not only the the yield of paneer would be increased, but also the loss of nutritious milk solids in the whey could be minimized.

4. LONG LIFE UF PANEER - A BREAKTHROUGH IN MODERN TECHNOLOGY

An innovative approach employing 'in-package' sterilization directed at heat/acid coagulation of ultrafiltered milk coupled with texturization, therefore, has been conceptualized (Rao, 1991). The schematic diagram for the manufacture of paneer employing Ultrafiltration is given in Fig. 1.

The whole milk was standardized as per the required fat content and it was fed to the ultrafiltration unit. A laboratory module of hollow fibre membrane (Romicon Membrane, type PM-50, Fibre inner diameters 0.9 mm, effective area 2.5 m², Alfa-laval, Denmark) was used for ultrafiltration. After the addition of acidulants and other additives, the ultrafiltered milk is filled into the retort pouches and were subjected to thermal texturization. The newly developed technology would permit total mechanization of process suitable for industrial manufacture of long life paneer.
Whole Milk → Standardized Milk → Concentration by Ultrafiltration → Chilling → Acidulant/Additives → Pouch Filling → Thermal Texturization → UF Paneer → Storage

Cream (By product)

Fig. 1 Schematic diagram for the manufacture of Long Life UF Paneer
4.1. SALIENT FEATURES OF NEW TECHNOLOGY

The salient features of the new technology are:

i. A process has been developed which permits integration of newly developed energy efficient unit processes into a system for fully mechanized continuous manufacture of paneer on commercial scale.

ii. The process permits enhancement of shelf-life upto 3 months at room temperature suitable for organized marketing in tamper-proof attractive packages.

iii. The process permits conservation of all milk solids without loss of any whey, thus, avoiding any problems of pollution or waste of nutrients.

iv. The process allows enhancement of yield of paneer to 30% in comparison with traditional process which allows a yield of only 15%.

v. The process maintains the utmost of hygienic quality and product safety attainable through modern technology.

vi. The cost of manufacture of the product is estimated about Rs. 18 per kg in comparison with Rs. 28 to Rs. 35 per kg of the conventional paneer.

vii. The consumers' response in Delhi and Karnal has been very favourable, indicating an excellent future industrial potential.

5. REFERENCES


1. INTRODUCTION

Shrikhand is a fermented and coagulated Indian milk product which is especially popular as dessert or pudding in western India. The intermediate product obtained by draining of dahi (curd) for preparation of shrikhand is called chakka. This is similar to "Quark", but not comparable due to its high dry matter contents, i.e., 26% (Patel and Chakraborty 1985). Traditionally, chakka is prepared by draining the whey from lactic fermented dahi obtained either from cow’s or buffaloe’s milk. It has a closely knit plastic body and texture and acidic diacetyl flavour. Colour varies from yellowish white to marble white depending on the type of milk used and is the base material for making shrikhand. Shrikhand is made by mixing cream and sugar with skim-milk chakka so as to get a final composition, i.e. fat 6%, SNF 13% and sucrose 41% (Patel and Chakraborty; 1985). In chakka, high fat cream and sugar are mixed properly with a planetary mixer at 30 to 35 rpm for half an hour to get a product with smooth texture, plastic body, a sweet-acidic flavour. Addition of saffron aroma and colour are optional. This is then finally called shrikhand.

This is a product which is made by housewives in western India at very small scale for home consumption, however, successful attempts have been made to develop an industrial process for the manufacture of shrikhand (Aneja et al., 1977)

The traditional technology allows the whey proteins to drain along with whey during the process of chakka making. These proteins, having high biological value could be recovered in chakka by the application of ultrafiltration to make, so called UF-chakka. This UF-chakka could be handled in similar manner as traditional chakka to make the final product, i.e. shrikhand. With this basic idea, an attempt has been made to make UF-shrikhand. There are two main advantages of such a process: (i) higher yield of chakka, because of recovery of whey proteins, and (ii) easy automation and process control.

2. PROCESS TECHNOLOGY

2.1. Raw milk

Raw cow’s milk was obtained from Research Centre’s dairy farm and was separated. Skim-milk so obtained was used for making chakka.

2.2. Coagulation of skim milk

Skim-milk was heated in a double jacketed vat with slow agitation upto a temperature of 95° C for 5 min. Then it was cooled to 21-22° C and inoculated with mixed starter culture (i.e. Streptococcus lactis, S. cremoris and S. diacetylactis) at the rate of 0.1-0.15%. It was incubated at 21-22° C for 16-18 hrs so as to get curd with pH of 4.6-4.5 and with a pleasant diacetyl aroma. Rapid fermentation could be done with
yoghurt culture (Streptococcus thermophilus and Lactobacillus bulgaricus) requiring 4 hours of incubation as suggested in the literature (Patel and Chakraborty, 1985).

2.3 Chakka making

Chakka from above coagulated milk was made by the traditional method and also by ultrafiltration as shown in the process flow charts (Fig.1 and 2).

```
Skim-milk  
↓  
Heated to 95° C for 5 min  
↓  
Cooled to 21-22° C  
↓  
Inoculated with starter culture  
(0.1-0.15%)  
↓  
Incubated for 16-18 hrs  
at 21-22° C  
↓  
Coagulated milk  
(pH 4.6-4.5)  
↓  
Whey drained through  → Whey  
a muslin cloth  
↓  
Chakka
```

Fig.1 Chakka by traditional process

2.4 Ultrafiltration Unit

Ceramic filtration module (NO.P-19-40) manufactured by Cerver Company (France) was used for ultrafiltration. The specifications of the module are given in Table 1. The ultrafiltration setup was designed at this Institute with a centrifugal pump of 5,000 litres/hr capacity so as to obtain a velocity of 5 m/sec in the module. The setup is shown in Fig.3. Operating conditions of ultrafiltration were: temperature = 50 ± 2°C; transmembrane pressure, i.e. 0.5 (pi + po) = 4 bars; where pi and po are inlet and outlet pressures of the module respectively. For every trial a fixed quantity of skim-milk curd was taken for ultrafiltration up to a predetermined concentration factor (CF) = 4. The UF-plant was cleaned with a combination of water flushing, hot alkali (Ultrasil-25) at 75°C and acid (Ultrasil-75) at 50°C circulation, at inlet and outlet pressures of 4 and 2 bars respectively. The plant was said to be clean only when it regained its original water flux.
Skim-milk

↓
Heated to 95° C for 5 min

↓
Cooled to 21-22° C

↓
Inoculated with starter culture
(0.1-0.15%)

↓
Incubated for 16-18 hrs
at 21-22° C

↓
Coagulated milk
pH (4.6-4.5)

↓
Agitated with slow speed
stirrers in the vat

↓
Slowly heated to 60-62° C for 5 min

↓
Cooled to 50° C

↓
Ultrafiltration ——————> Permeate
at 50 ± 2° C

↓
UF-concentrate (19.2% TS)

↓
Pressing ——————> Whey

↓
chakka

Fig. 2 Chakka by ultrafiltration process

Table 1: Specifications of Ceramic Modules

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>No. P-19-40</td>
</tr>
<tr>
<td>Material</td>
<td>-Al₂O₃</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>0.2 μm</td>
</tr>
<tr>
<td>Membrane surface area</td>
<td>0.2 m²</td>
</tr>
<tr>
<td>Number of channels</td>
<td>19</td>
</tr>
<tr>
<td>Length of channels</td>
<td>850 mm</td>
</tr>
<tr>
<td>Channel diameter</td>
<td>4 mm</td>
</tr>
<tr>
<td>Maximum pressure</td>
<td>8 bars</td>
</tr>
<tr>
<td>Permeability to water at 20° C</td>
<td>3000 l/h m²</td>
</tr>
</tbody>
</table>
2.5. Shrikhand Making

Chakka obtained either by traditional or ultrafiltration method was mixed with 70% fat cream and sugar, so as to get approximately the same composition suggested to be the best in literature (Patel and Chakraborty, 1985), i.e. fat 6%, sugar 41% and moisture 40%. The mixture was kneaded with clean hands at 25-26° C in order to get a smooth paste like semisolid consistency with no feeling of sugar grains. The process flow diagram is given in Fig.4.

Chakka
(traditional or UF)
\[ \downarrow \]

Addition of 70% fat cream and sugar
\[ \downarrow \]

Kneading in a small kettle by hand
\[ \downarrow \]

Filling in cups
\[ \downarrow \]

Cooling to 10-12° C
\[ \downarrow \]

Shrikhand

Fig. 4 Shrikhand from Chakka

2.6. Sampling and analytical methods

Samples of chakka, whey, permeate and shrikhand were taken for analysis of total solids, protein lactose and calcium. The samples were analysed for total solids by gravimetric method. Protein content was taken as 6.38 times the nitrogen content determined by Kjeldahl analysis. Calcium and lactose were determined by Technico auto-analyzer. The pH was measured by a digital pH meter.

2.7. Sensory evaluation

The samples of shrikhand were judged by a panel of judges. The scores were given on 9-point hedonic scale, ranging from 9 (liked extremely) to 1 (disliked extremely).

3. PROCESS ECONOMICS

3.1. Average flux during ultrafiltration of coagulated skim-milk

The average flux started at a very high level of 165.4 l/h m² and slowly declined to an average level of 86.13 l/h m² so as to get a concentration factor (CF) =4. This is a very high flux which is only obtainable with ceramic membranes with high pressure (4 bar) and high velocity (5 m/sec) conditions at 50 ±2° C. The average protein retention coefficient of this membrane with coagulated skim-milk was 0.98.
3.2. Mass balance and recovery of total solids (TS) in chakka

By traditional method, 100 kg of coagulated skim milk of 9% TS after draining through muslin cloth gave on an average 88.08 kg of whey with 6.7% TS and 11.91 of chakka with 26% TS. This worked out to be 34.44% recovery of total solids of milk as chakka. The systematic calculations are diagrammatically shown in Appendix I. Losses of total solids in whey were very near to losses reported in literature.

Ultrafiltration of coagulated skim milk and after pressing of UF-coagulated milk retentate gave a chakka of the same total solids as above. 100 kg of coagulated skim milk was concentrated using ultrafiltration to a concentration of 19.2% TS. This gave on an average 75 kg of permeate with 5.6% TS and 25 kg of UF coagulated milk retentate of 19.2% TS. The UF coagulated milk retentate was pressed so as to remove 9.2 kg of whey with 7.58% TS and finally gave on an average 15.5 kg of UF-chakka with 26% TS. This worked out to be 45.24% total solids recovery as against 34.4% by the traditional method. Systematic calculations are given in Appendix II.

3.3 Extra yield of chakka

Yield of chakka obtained by traditional and UF-method from 100 kg of coagulated skim-milk were 11.91 and 15.5 kg respectively. Therefore, percentage extra yield is:

\[
\frac{15.5-11.91}{11.91} \times 100 = 23.16\%
\]

\[
\frac{15.5}{11.91} = 1.28\%
\]

\textit{Saving in coagulated skim-milk:} Kg of coagulated skim-milk required for one kg chakka

a) Traditional method \(\frac{100}{11.91} = 8.39\)

b) UF-method \(\frac{100}{15.50} = 6.45\)

Therefore, saving of coagulated skim-milk per kg chakka prepared was \((8.39-6.45) = 1.94\) kg. And percentage saving of coagulated skim-milk was worked out to be

\[
\frac{1.94}{11.91} \times 100 = 16.28\%
\]

It means 16.18% less coagulated skim-milk shall be required for making chakka by the new ultrafiltration method. The saving is because of the recovery of whey proteins, and a slightly higher lactose in chakka.

3.4. Sensory quality of shririkhand

Shrikhand was made by using traditional and UF-chakka so as to obtain 6% fat, 41% sugar and 40% moisture. It was subjected to a panel of judges. The average scores for traditional and UF-shrikhand were 7 and 6.5 on a 9 point hedonic scale respectively.

\textbf{Table 2:} Comparison between traditional and ultrafiltration method of chakka production
<table>
<thead>
<tr>
<th>Chakka making process</th>
<th>Traditional</th>
<th>UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chakka TS%</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Skim milk, pH 4.6 - 4.5, TS%</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Skim milk, protein %</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Whey or permeate TS%</td>
<td>6.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Skim milk/Chakka kg/kg</td>
<td>8.39</td>
<td>6.45</td>
</tr>
<tr>
<td>Milk saving %</td>
<td>0</td>
<td>16.28</td>
</tr>
<tr>
<td>Extra yield %</td>
<td>0</td>
<td>23.16</td>
</tr>
</tbody>
</table>

Judges gave less scores, because they did not like a high level of sugar; however, there was practically no difference in traditional and UF shrikhand. The judges liked it as pudding or dessert and as an after food delicacy.

4. CONCLUSION

It is possible to make shrikhand of very good quality by UF chakka. This process is an industrially feasible process and provided 16.28% milk saving and easy automation and process control. In India, there is sufficient scope for adopting this ultrafiltration method for making shrikhand.

5. REFERENCES

Flow Rate and Temperature with Devices for Measuring Pressure

Diagram of Ultrafiltration Unit

1. Feed tank
2. Circulation pump
3. Feed valve
4. Thermometer
5. Flow meter
6. Pressure gauge
7. Membrane module
8. Deaerating valve
9. Heat exchanger
10. Bleed valve
11. BY-PASS valve
P Retentate
W Permeate
W Water

Figure 3
APPENDIX 1: Mass balance of chakka making by traditional method

<table>
<thead>
<tr>
<th>Whey</th>
<th>80.08 kg (6.7% TS)</th>
<th>TS = 5.90 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draining through muslin cloth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chakka</td>
<td>11.91 kg (26% TS)</td>
<td>TS = 3.1 kg</td>
</tr>
</tbody>
</table>

APPENDIX 2: Mass balance of chakka by ultrafiltration method

<table>
<thead>
<tr>
<th>Permeate</th>
<th>75 kg (5.6% TS)</th>
<th>TS = 4.2 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UF coagulated skim milk retentate</td>
<td>25 kg (19.2% TS)</td>
<td>TS = 4.8 kg</td>
</tr>
<tr>
<td>Permeate in muslin cloth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chakka</td>
<td>15.5 kg (26.3% TS)</td>
<td>TS = 4.08 kg</td>
</tr>
</tbody>
</table>
MANUFACTURE OF LOW LACTOSE POWDER USING ULTRAFILTRATION TECHNOLOGY

Dr. R. S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132001

1. INTRODUCTION

Lactose, a disaccharide composed of glucose and galactose is the major solids component of milk. Before it can be absorbed by man it must be broken down into its components by the enzyme lactase, a membrane-bound enzyme present in the brush border of the small intestines epithelial cells (Fernandes and Shahani 1989). It is known that the lactase enzyme is deficient in much of the world's population. If the amount of lactose ingested exceeds the hydrolytic capacity of the available intestinal lactase, a portion of the lactose remains undigested and is transported into the large intestine. Undigested lactose in the large intestine increases the osmolality of the intestinal fluid and thus draws from the tissues into the intestine. Undigested lactose may also be fermented by bacteria in the colon thus generating organic acids, carbon dioxide and hydrogen, these fermentation products together with the large amount of water drawn into the intestine are largely responsible for various symptoms, like bloating, flatulence, abdominal cramps, diarrhoea and loss of appetite (Fernandes and Shahani 1989, Patel et al., 1994)

Lactose intolerance is a global problem. There are people with total lack of lactase activity or very small amounts of this enzyme, others with a normal amount and activity of lactase. In the middle zone with moderate lactase activity one can find people with transitory symptoms for example with diarrhoea after excessive intake of milk once or twice in their life. On the other hand, some people with low lactase activity tolerate milk well, when they drink it in small quantity (Kocin 1988).

2. NUTRITIONAL COMPLICATIONS OF LACTOSE INTOLERANCE

People who avoid dairy foods due to perceived lactose intolerance may not be getting enough dietary calcium and a number of other important nutrients like phosphorus, magnesium, riboflavin, provided by dairy foods. Also, due to unavailability of lactose, calcium absorption in the body becomes very difficult. It is postulated that lactose complexes calcium or other metals and increases absorption. Also, lactose moieties, glucose and galactose, enhance calcium absorption when released into ideal segments. Lactose also increases absorption or retention of other minerals.

Inadequate calcium intake due to lactose intolerance may be linked to several medical conditions including poor skeletal growth, hypertension toxemia of pregnancy, colonic neoplasmia, and osteoporosis (Solomons 1981).
3. DIETARY MANAGEMENT FOR LACTOSE INTOLERANCE PEOPLE

Since dairy products are highly visible, popular foods in our culture, lactose in unaltered forms is difficult to avoid, even if eliminates or limits consumption of fresh dairy products. Crème soups, pudding cream pies, khoa based sweets, custards and ice-cream are not lactose free foods. Technologists and nutritionists are seeking effective methods to improve the tolerance of dairy products in lactose-deficient individuals either by hydrolysis of lactose in milk or reducing lactose by employing ultrafiltration technology (Miller and Brand, 1980; Patel et al., 1995).

Since most persons who are lactose intolerant are able to tolerate varying amounts of lactose, they have several options regarding consumption of dairy products. One option is determine one's threshold for the occurrence of symptoms associated with lactose intolerance and to consume less that amount of lactose. Another possible way is hydrolysis of lactose, because of the fact that the residual lactase activity is present even in lactose intolerance population, hence about 75% lactose hydrolysis takes care of most of the lactose intolerance cases. For hydrolysis of lactose, the lactase enzyme has to be added to milk some time before use (Miller and Brand 1980). However, there are certain problems associated with hydrolysed milk, like the resultant product is sweeter than original milk and has a slightly higher osmolality. Due to sweet taste its acceptance has been limited. Also unavailability of this type of milk in restaurants, and shops and the inconvenience of waiting 12 to 24 hours for hydrolysis of regular milk treated at home with commercially available enzyme preparations. Also, in developing and tropical countries the need for refrigeration during home hydrolysis presents another limitation. Keeping aforesaid problems in mind it does not seem to be an ideal solution of the problem.

Various methods have been developed to reduce the lactose concentration. These include crystallization, dialysis, gel filtration and ultrafiltration. Other methods aimed at chemically modifying the lactose molecule include reduction, oxidation, fermentation and hydrolysis (Millard and Brand, 1980). Lactose hydrolysis opens new possibilities for milk to be consumed by lactose intolerant individuals. However, there are some technological and nutritional problems. Because of lactose hydrolysis skimmed milk powder in particular has a tendency to stick to the hot metal surface of the spray dryer. The powder also lumps in the cone and star valve unless cooled with forced dry air as it leaves the cone. There is also a considerable reduction in protein quality in lactose hydrolysed milk powder, mainly because of the loss of biologically available lysine. The loss increased during storage, due mostly to non-enzymatic browning. The glucose and galactose resulting from hydrolysis of the lactose have high mobility in media with low water activity and react more readily with the amino groups of the proteins than does the disaccharide (Sanjose et al., 1977)

Ultrafiltration technology can be employed for the manufacture of low-lactose powder since this powder is the easiest to produce. The production method simply consists of the ultrafiltration of milk followed by the drying process.

The milk of animals has been an age-old traditional food for many and it is a major source of calcium, protein and riboflavin. However, populations from non-dairy cultures such as Arabs, Chinese, Indonesians, Koreans, Vietnamese, Africans and
South Americans are unable to digest milk due to lactase deficiency. In this research work attempts were made to remove lactose from the milk system, by employing ultrafiltration technology. In order to remove or reduce lactose from milk the skimmed milk was first pasteurized at 71°C/16 s, and then ultrafiltered to 5.5-fold concentration (Fig. 1). The retentate obtained had a composition of 24.52 % total solids, 17.99 % protein, 4.21% lactose and 2.33 % ash (Table 1). However, this retentate still had a fairly high level of lactose and since the main aim was to reduce the lactose content as far as possible, diafiltration was employed for its further removal. Distilled water at the rate of 50% of the retentate was added and ultrafiltration continued further. The retentate obtained had a composition of 22.76 % total solids, 18.01% protein, 2.55% lactose and 2.19% ash. The retentate was spray dried and the composition is shown in Table 1. The powder obtained had poor reconstitutability properties and was also criticized for a flat taste. In order to improve the drying properties of the retentate and reconstitutability of the powder, malto-dextrin was partially added at the rates of 4 % and 8% of retentate, and the mixture was spray dried. The composition of the two powders obtained is shown in Table 1.

Table 1. Composition of skimmed milk, retentate and low-lactose powders (%)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Total solids</th>
<th>Protein</th>
<th>Lactose</th>
<th>Ash</th>
<th>Malto-dextrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skimmed milk</td>
<td>9.31</td>
<td>3.32</td>
<td>5.1</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>Retentate I^1</td>
<td>24.52</td>
<td>17.99</td>
<td>4.21</td>
<td>2.33</td>
<td>-</td>
</tr>
<tr>
<td>Retentate II^2</td>
<td>22.76</td>
<td>18.01</td>
<td>2.55</td>
<td>2.19</td>
<td>-</td>
</tr>
<tr>
<td>Low-lactose powder I^3</td>
<td>96.73</td>
<td>66.01</td>
<td>9.3</td>
<td>6.89</td>
<td>14.94</td>
</tr>
<tr>
<td>Low-lactose powder II^4</td>
<td>96.89</td>
<td>56.31</td>
<td>7.97</td>
<td>6.6</td>
<td>26.21</td>
</tr>
<tr>
<td>Low-lactose powder III^5</td>
<td>96.36</td>
<td>38.15</td>
<td>5.4</td>
<td>4.93</td>
<td>44.89</td>
</tr>
</tbody>
</table>

^1 5.5 fold concentration of skim milk
^2 Obtained after diafiltration (1:0.50 W/W)
^3 Spray drying of retentate II mixed with malto-dextrin at the rate of 4% of retentate.
^4 Spray drying of retentate mixed with malto-dextrin at the rate of 8% retentate.
^5 Dry mixing of malto-dextrin with low lactose powder

Table 2. Composition of Cow’s milk, UF concentrate and low-lactose powders (%)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Milk</th>
<th>Retentate I</th>
<th>Retentate II</th>
<th>Low lactose powder I</th>
<th>Low lactose powder II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids</td>
<td>13.39</td>
<td>37.82</td>
<td>36.79</td>
<td>96.03</td>
<td>96.55</td>
</tr>
<tr>
<td>Protein</td>
<td>3.44</td>
<td>12.93</td>
<td>13.09</td>
<td>31.54</td>
<td>28.68</td>
</tr>
<tr>
<td>Fat</td>
<td>4.25</td>
<td>19.15</td>
<td>18.6</td>
<td>44.83</td>
<td>38.4</td>
</tr>
<tr>
<td>Lactose</td>
<td>4.9</td>
<td>4.1</td>
<td>2.51</td>
<td>6.04</td>
<td>5.5</td>
</tr>
<tr>
<td>Ash</td>
<td>0.79</td>
<td>1.64</td>
<td>1.59</td>
<td>3.82</td>
<td>3.48</td>
</tr>
<tr>
<td>Malto-dextrin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
<td>21.66</td>
</tr>
</tbody>
</table>

^1 4.5 fold concentration of milk
^2 Obtained after diafiltration (1:0.50 W/W)
^3 Spray drying of retentate II mixed with malto-dextrin at the rate of 4% of retentate.
^4 Dry mixing of malto-dextrin with low lactose powder I
Fig 1. The procedure for the manufacture of low-lactose powder

The reconstitutability properties of the powder which had maltoextrin added to the retentate before drying were found to be much better than those for the one which was dried as such. However, there was not much difference between the reconstitution properties of powder with 4% and 8% added malto-dextrin. Hence, addition of 4% malto-dextrin to the retentate is recommended. In order to restore the sweetness in milk higher quantities of malto-dextrin were required, which were dry blended with the low-lactose powder. During the ultrafiltration process, some of the soluble salts like calcium, sodium and potassium are bound to go in the permeate. These salts are important for giving milk its natural taste. To maintain the salt level and thereby revive the original taste of milk on reconstitution, salts were added to the retentate before spray drying. Varying quantities (0.75, 1.0, 1.25 and 1.50 %) of a salt mixture of KCl and citrate in the ratio of 1:0.77 as suggested by Edelsten et al. (1983) were added to the retentate to arrive at an optimal level. The mixture was reconstituted to 9% total solids and subjected to sensory evaluation, taking fresh milk as a control. It was observed that a salt level of 1.0% gave a powder which on reconstitution was close to fresh skimmed milk. However, it was criticized for its powdery flavour and it was slightly lacking in natural taste of milk. In order to accentuate the flavour, natural flavourings (viz., vanilla, banana, chocolate and maracuja) were added. It was observed that the banana and vanilla flavours gave better, acceptability scores in the reconstituted low-lactose powder as compared to chocolate and maracuja flavours. This low-lactose powder had a composition of 96.36 % total solids, 38.15 % protein, 5.40 % lactose, 4.93 % ash and 44.89 % maltodextrin. The low-lactose powder was also manufactured from whole cows' milk. The manufacturing process was the same as for skimmed milk low-lactose powder. The final composition of the low-lactose powder obtained was: 96.55 % total solids, 28.68 % protein 38.40 % fat, 5.50 %
lactose, 3.48% ash, and 21.66% malto-dextrin (Table 2). The overall quality of the powder was better than the powder obtained from skimmed milk.

4. TIPS FOR LACTOSE INTOLERANT PEOPLE

Several studies suggest that lactase non-persistent individual may digest fermented dairy foods more efficiently, as they provide lactase produced by bacteria during fermentation (Shahani and Chandan, 1979; Fernandes and Shahani 1989). Recommendation can be made for consumption of many hard varieties of cheeses as they contain only small amount of lactose and can normally be consumed by lactose deficient individuals, without any ill-effects. Among cheeses matured Cheddar has the lowest lactose content. People from Asian continents can consume paneer and channa based products since these products possess less amount of lactose.

The other possibility is to use low-lactose powder. The powder can be reconstituted to 10% total solids level and can be used by lactose intolerant people without any ill effect.

In 1987 a conference on translating research information on lactose intolerance was arranged by the National Dairy Council in Illinois. They have brought out a few important observations related to lactose-intolerance, which I would like to report here for the readers of this lecture note.

(i) Most persons who have difficulty in tolerating milk do not need to give up dairy foods entirely. However, those persons can modify the types of dairy foods consumed, serving sizes and frequency of dairy foods consumption to alleviate or eliminate symptoms.

(ii) Whole milk is tolerated better than skim milk by lactose intolerant persons. (3) There is some preliminary evidence that chocolate milk may be tolerated better than unflavored milk by lactose intolerance persons.

(iii) Yoghurt containing active cultures is tolerated better than milk by lactose intolerant person.

(iv) Yoghurt containing active cultures is tolerated better than yoghurt with no active cultures by lactose intolerant persons due to the inherent lactase activity of the culture.

(v) Most cheeses and hard cheeses in particular, have a low lactose content and are better tolerated than milk by lactose intolerant persons

(vi) Many individuals who are lactose intolerant can better tolerate milk taken with meals or other foods than milk consumed alone.

(vii) Person who have difficulty in digesting lactose can tolerate smaller and more frequent serving of milk better than large, less frequent servings.

(viii) Lactose intolerance may be improved by gradually increasing lactose consumption over the time.

(ix) Some dairy products such as milk and ice-cream can be specially modified to reduce the lactose content. These lactose reduced dairy products are available commercially in many countries.
6. REFERENCES


Lea, C. H. and Rhodus, D. N. (1952) Studies of the reaction between proteins and reducing sugars in the dry state. V. The reactions of D-galactose, 2-deoxy-D-galactose, D-glucosamine and N-acetyl D-glucosamine was casein. Biochemica Biophysica Acta, 9, 56-60


APPLICATION OF REVERSE OSMOSIS IN DAIRY INDUSTRY

Dr. Dharam Pal
Dairy Technology Division, NDRI (ICAR), Karnal 132 001

1. INTRODUCTION

The use of reverse osmosis (RO) was first started in 1960's after the development of synthetic asymmetric membrane by S. Sourirajan. In its initial stage the RO process was mainly used for desalination and water treatment. The process gained entrance in food industry, particularly the dairy, in the seventies and its applications increased dramatically in the 1980's. RO is now considered as the most economic process of removing water from liquid foods including milk. At present there are more than 200 commercial RO plants worldwide in the dairy industry. The important applications of RO are listed below

• Concentration of whey and milk prior to evaporation
• Bulk transport of raw milk
• Speciality milk products

2. PROCESSING OF WHEY

The production of cheese, pance and casein, create large volumes of whey (approximately 80-90% of the initial volume of milk). Whey contains between 5.5 and 6.5% solids that have a proximate composition (dry basis) of 12% protein, 1% fat, 70-75% lactose, 8-10% inorganics and 0.1-1.0% lactic/citric acid. The presence of many valuable milk constituents (protein and lactose), and its huge pollution load (30,000-50,000) ppm B.O.D. justify the need for economic processing of whey. However, the large proportion of water in the whey makes its processing energy intensive, per unit of solids, compared with other dairy processes. Operations such as pumping, transportation, concentration, fractionation and drying, all use more energy per unit of product than the dairy industry can afford.

RO has the potential for removing a major part of the water from whey more economically than other evaporative process (Table 1)

RO may be used (a) as a preconcentration step prior to transportation of whey and (b) for its concentration for using as such or for making whey products. Whey can be easily concentrated to about 18% total solids on a batch type RO plant, but with the use of multistage recycle designs (MSR), concentration up to 26-28% total solids is now technically and economically feasible. Flux for RO of whey is normally higher than that for milk mainly because of lower total solids in the former.
Table 1: Energy Cost of Efficient Evaporation vs Reverse Osmosis for Whey

<table>
<thead>
<tr>
<th>Energy per tonne of whey</th>
<th>Efficient evaporation</th>
<th>RO conc. to:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Stage</td>
<td>2 stage</td>
</tr>
<tr>
<td>Steam (tonnes)</td>
<td>0.62</td>
<td>0.14</td>
</tr>
<tr>
<td>Electricity (KWh)</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Total equivalent (KWh)</td>
<td>387</td>
<td>90</td>
</tr>
<tr>
<td>Equivalent energy</td>
<td>192</td>
<td>46</td>
</tr>
</tbody>
</table>

Initial total solid in whey = 6%
MVR - Mechanical vapour recompression
TS - Total solids

The following pretreatments of whey are necessary for improved performance of the RO plant.

- Raw whey obtained from cheese and paneer making operations should be centrifuged or microfiltered to remove casein fines and fat globules.

- Heating whey to about 80°C improves the flux and bacterial quality.

- Adjusting pH of whey to either 3.0 or 7.0 followed by centrifugation and addition of calcium sequestering agent (EDTA) or its demineralization significantly reduce the fouling problems.

The concentrated whey and whey products such as whey powder, whey proteins, powder demineralized whey powder and lactose, have several applications in the food industry, for example, in bakery products confections and candies, processed cheese products, frozen desserts, yoghurt and fermentation products.

3. CONCENTRATION OF UF PERMEATE

Applications of ultrafiltration (UF) process in concentration and fractionation of whey, skim milk and whole milk are increasing rapidly for various purposes, particularly for cheese making. Consequently, a large quantity of permeate is produced as a by-product. The UF permeates contain 5.5-6.5% solids of which approximately 85% is lactose alone and 8-9% are minerals. Such a high concentration of lactose obviously suggests the potential use of UF permeate in the manufacture of lactose.

Presently lactose is prepared by concentration, fractionation, crystallization and centrifuging of cheese or casein whey. Whey and UF permeate are dilute solutions of lactose (5.0 to 5.5%). For getting higher yield and better purification, concentration of whey and UF permeate up to 50% total solids before crystallization is desirable. Thus, RO can play an important role in concentrating UF permeate with minimum energy requirements and least thermal degradation. It is possible to concentrate UF milk permeate from initial total solids of 5.8% to about 25% by RO and maintain a reasonable flux. Higher concentration than this may not be economically feasible with
the present generation of membranes and current energy costs. This is due to the flux resulting from osmotic pressure limitations arising from the concentration of solutes (mainly lactose and minerals) in the feed.

The quality of lactose can be improved by demineralization of permeate using nanofiltration process before the RO. About 98-99% of COD of the UF-permeate is retained in the concentrated product. Therefore, the permeate from the RO processing is free from any organic matter and thus a permissible waste.

4. CONCENTRATION OF MILK

Several factors influence the performance of RO unit and the quality of product. Some of these, particularly, the operating parameters (pressure, temperature, feed concentration and flow rate) are already discussed. Others are given here.

- The results of a typical survey of RO plant having CA membrane, showed that first portion of product coming out of plant had high standard plate count. This problem however, was less serious in plants having non-cellulosic membrane. The RO plant therefore requires a proper cleaning and sanitizing cycle immediately before each run for getting a product of satisfactory quality.

- The second problem relates to damage of fat globules resulting in release of free fat. This is due to the shearing action of the high pressure pumps in RO unit causing distinct homogenization action on milk fat. If lipase enzyme is not inactivated before RO processing, the hydrolysis of fat take place leading to spontaneous development of rancid flavour in milk.

These problems have been solved by modification of the RO unit and giving suitable heat treatment, preferably, the thermization or pasteurization to the milk (Table 2). The use of restriction pipe of smaller diameter instead of pressure control value in the retentate line and the cooling of retentate below 10°C before pressure release have also helped controlling the release of free fatty acid. In addition to the above benefits, heating of milk prior to its RO process decrease the fouling of membrane and improve the flux.

Table 2. Effect of Reverse Osmosis Process (at 30°C Using cA Membranes) on Bacteriological Quality and Free Fatty Acids Levels of Whole Milk.

<table>
<thead>
<tr>
<th>Concentration Ratio</th>
<th>Bacterial Count</th>
<th>Free fatty acids (mili equiv/100 g fat)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw milk</td>
<td>Heated milk*</td>
</tr>
<tr>
<td>1.0</td>
<td>4.1 x 10^2</td>
<td>1.4 x 10^2</td>
</tr>
<tr>
<td>1.5</td>
<td>1.8 x 10^4</td>
<td>2.1 x 10^2</td>
</tr>
<tr>
<td>2.0</td>
<td>2.6 x 10^4</td>
<td>4.3 x 10^2</td>
</tr>
<tr>
<td>2.5</td>
<td>2.8 x 10^4</td>
<td>5.1 x 10^2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Raw milk</th>
<th>Heated milk*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>1.5</td>
<td>9</td>
<td>2.3</td>
</tr>
<tr>
<td>2.0</td>
<td>10.2</td>
<td>1.7</td>
</tr>
<tr>
<td>2.5</td>
<td>10.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

* Milk heated to 80°C for RO
The flux is dependent on the characteristics of membranes and feed, and the levels of concentration. The non-cellulosic membrane gives higher flux (Table 3) as well as better rejection properties. Fig. 1 shows the effect of solids concentration on the flux using optimum operating conditions. Since the system is operating in the mass transfer controlled region, the relationship between flux and solids concentration appears to follow the film theory. The difference between the three milks is due to slight difference in their initial composition, pretreatment and fouling of membrane. By extrapolation it appears that maximum concentration that can be obtained for whole milk is 38% TS and for skim milk 28% TS. These levels also can not be considered as economical because the flux is almost negligible at this stage. The economic levels of RO concentration for skim milk is 22% TS and for whole milk up to 30% TS.

Table 3. Average flux of different milk systems

<table>
<thead>
<tr>
<th>Milk Systems</th>
<th>Type of membrane</th>
<th>Temp. (°C)</th>
<th>Level of conc.</th>
<th>Average Flux (L/m²/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skim milk</td>
<td>CA-97</td>
<td>30</td>
<td>2.8</td>
<td>11.5</td>
</tr>
<tr>
<td>skim milk</td>
<td>PA-99</td>
<td>50</td>
<td>2.8</td>
<td>19</td>
</tr>
<tr>
<td>skim milk</td>
<td>ZF-99 (Composite)</td>
<td>50</td>
<td>2.8</td>
<td>23</td>
</tr>
<tr>
<td>UF permeate</td>
<td>CA-97</td>
<td>30</td>
<td>4</td>
<td>20.5</td>
</tr>
<tr>
<td>Cow milk</td>
<td>CA-97</td>
<td>30</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Cow milk (Homogenized)</td>
<td>CA-97</td>
<td>30</td>
<td>3</td>
<td>8.9</td>
</tr>
<tr>
<td>Buffalo milk</td>
<td>TFC-99</td>
<td>50</td>
<td>2</td>
<td>23</td>
</tr>
<tr>
<td>Buffalo milk</td>
<td>TFC-99</td>
<td>50</td>
<td>1.5</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig. 1. Relationship between total solids and flux during reverse osmosis of milk. (△= skim milk; ○= whole milk; ◯= homogenized whole milk). The transmembrane pressure was 400 psig and the flow rate (Q) was 12 L/min.
The effect of RO processing on the chemical composition of whole milk is given in Table 4 below.

Table 4: Composition of RO concentrated whole milks

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Buffalo Milk*</th>
<th>Cow milk**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>2.0 X</td>
</tr>
<tr>
<td>Total solids</td>
<td>16.57</td>
<td>32.88</td>
</tr>
<tr>
<td>Fat</td>
<td>6.05</td>
<td>12.05</td>
</tr>
<tr>
<td>Protein</td>
<td>4.6</td>
<td>9.12</td>
</tr>
<tr>
<td>Ash</td>
<td>0.78</td>
<td>1.35</td>
</tr>
<tr>
<td>Lactose</td>
<td>5.28</td>
<td>10.43</td>
</tr>
</tbody>
</table>

* Type of membrane used TFC-99
** Membrane used CA-97

Rejection of fat and total proteins in both types of membranes, cellulose and composite has been observed as 100%. Slight loss of NPN, ash and lactose in permeate using CA-97 membrane has been reported at concentration level above 2.5%.

5. APPLICATIONS OF RO PROCESSED MILK

5.1 Bulk transportation of RO concentrated milk:

The transportation of milk in "single strength" is very expensive. The feasibility of transporting raw milk from rural chilling centres in concentrated form to city dairies was studied. There was no loss of milk solids into permeate when buffalo whole milk was concentrated milk, upto 2 fold. The quality of RO concentrated milk during transportation at 4±1°C is given in Table 5.

Table 5: Physico-chemical and microbial quality of RO concentrated milk on storage at 4±1°C

<table>
<thead>
<tr>
<th>Quality Attributes</th>
<th>Control Milk</th>
<th>2 X RO concentrated milk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fresh</td>
</tr>
<tr>
<td>Acidity (% L.A.)</td>
<td>0.18</td>
<td>0.4</td>
</tr>
<tr>
<td>pH</td>
<td>6.73</td>
<td>6.46</td>
</tr>
<tr>
<td>Viscosity (Cpat 20°C C)</td>
<td>2.38</td>
<td>24.82</td>
</tr>
<tr>
<td>FFA (meq/g)</td>
<td>1.82</td>
<td>3.2</td>
</tr>
<tr>
<td>Free fat (% of total fat)</td>
<td>6.78</td>
<td>0.58</td>
</tr>
<tr>
<td>cfu 4 x 10^5/ml</td>
<td>18.54</td>
<td>24.7</td>
</tr>
<tr>
<td>Fat globule size(range in μ)</td>
<td>5.7-11.4</td>
<td>1.9-2.5</td>
</tr>
</tbody>
</table>
The energy required for concentrating buffalo milk to 1.5 and 2-fold levels were 369.7 and 470.9 kJ/kg of water removed respectively. The corresponding costs were 3.69 paisa and 4.64 paisa for every kg of water removed. A saving of more than 25% in transportation cost by transporting milk in RO concentrated (2-fold) form were worked out. Saving upto 50% has been reported elsewhere.

### 5.2 Utilization of RO milk in fluid form

The RO concentrated whole milk can be used in the manufacture of certain fluid products like plain milk, flavoured milk, skim milk and high protein milk. The processes involve concentration of whole milk to about 2-fold, storage for 24 hours at 5°C, dilution with water to the composition of natural milk or to that desired, pasteurization, homogenization, addition of flavours, etc. Taste panels or the various liquid dairy products have shown that the majority (106 out of 111) could detect no significant effect attributable to inclusion of RO processing and later dilution with water on the organoleptic quality of any of the subsequent products. The effect on vitamin levels in milk due to RO process was negligible. Bacterial counts on control milk and reconstituted RO concentrates after pasteurization and during storage showed no significant difference. The shelf life of reconstituted milk was about 9-12 days under refrigerated conditions.

The RO concentrates could also be used as such after pasteurization and packaging. The keeping quality of the pasteurized RO concentrates remain almost similar to other dairy products. In a study where pasteurized RO concentrate (about 23-24% TS) was distributed for household evaluation in Australia, the respondents returned 67% favourable, 22% neutral and 11% negative attitudes to the product. The results of the study conducted on buffalo milk RO processing and its utilization in fluid form are shown in Table 6.

<table>
<thead>
<tr>
<th>Type of Milk</th>
<th>Flavour Score (Perfect Score 45)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
</tr>
<tr>
<td>Control (Fresh Buffalo Milk)</td>
<td>43.7</td>
</tr>
<tr>
<td>Diluted 2 X RO Milk</td>
<td>43.6</td>
</tr>
<tr>
<td>Conc. 2 X RO Milk</td>
<td>43.2</td>
</tr>
<tr>
<td>Diluted 1.5 X RO Milk</td>
<td>43.6</td>
</tr>
<tr>
<td>Conc. 1.5 X RO Milk</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Studies conducted on UHT processing of diluted RO milk and 2 fold RO concentrated milk showed very encouraging results. The preceding results indicates that the dairy industry can confidently explore the application of RO technology for concentrating whole milk at the collection/chilling centre followed by processing in fluid form at the city plant with its potential saving in transport cost. In addition, the water obtained during concentration of milk from RO plant is of high purity and can be used for drinking purpose.
5.3 Khoa from RO concentrates

Khoa, an important indigenous Indian milk product, is presently manufactured on a small scale by continuous boiling of whole milk until a desirable solids concentration (65-70% total solids) is reached. In recent years, several attempts have been made to develop new methods for commercial production of khoa, including the use of scraped surface heat kettles or heat exchangers evaporation for partial moisture removal and use of dried milk. The use of concentrated milk having upto 30% TS has produced khoa of highly satisfactory quality. Many commercial dairies are presently using concentrated milk for khoa making. The application of reverse osmosis being energy effective process, for pre-concentration of milk prior to the manufacture of khoa have great potential in India. We have prepared khoa from cow milk as well as buffalo milk using RO process. The cow milk was pasteurized at 63°C for 30 min, cooled to 30°C and concentrated on a spiral wound cA membrane module to two concentration levels i.e. 2x and 2.5x. In case of buffalo milk PC1-non cellulose acetate membrane constituted in a tubular module was used for concentration at 50°C upto 1.5x and 2.0x levels. Finally khoa was prepared by atmospheric boiling of RO retentates in a steam kettle (Fig.2).

![Diagram](image-url)

**Fig. 2 Manufacture of Khoa using the Cheryan-Pal RO process**

The chemical composition and sensory properties of khoa obtained by RO process are presented in Table 7. The most important difference in control khoa and RO khoa was the higher moisture retention and lower free fat content in the later. Use of highly concentrated milk adversely affect the flavour quality. The process is conveniently amenable to continuous production of khoa using SSHE in line with RO unit.
### Table 7 Composition and quality of khoa manufactured by RO process

<table>
<thead>
<tr>
<th>Proximate Composition (%)</th>
<th>Control Khoa</th>
<th>RO Khoa (24 %)</th>
<th>RO Khoa (30 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. COW MILK KHOA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>32.3</td>
<td>38.6</td>
<td>39.7</td>
</tr>
<tr>
<td>Fat</td>
<td>28.9</td>
<td>30.3</td>
<td>30.3</td>
</tr>
<tr>
<td>Protein</td>
<td>28.5</td>
<td>28.8</td>
<td>29</td>
</tr>
<tr>
<td>Ash</td>
<td>5.9</td>
<td>5.1</td>
<td>5</td>
</tr>
<tr>
<td>Lactose</td>
<td>36.7</td>
<td>35.8</td>
<td>35.6</td>
</tr>
<tr>
<td><strong>SENSORY QUALITY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flavour</td>
<td>Normal</td>
<td>Mild</td>
<td>Mild</td>
</tr>
<tr>
<td>Texture</td>
<td>Granular</td>
<td>Lack grains</td>
<td>Lack grains</td>
</tr>
<tr>
<td>Hunter Colorimeter Values</td>
<td>L=69.3</td>
<td>1=67.0</td>
<td>L=67.8</td>
</tr>
<tr>
<td></td>
<td>a=4.1</td>
<td>a=-1.5</td>
<td>a=-3.1</td>
</tr>
<tr>
<td></td>
<td>b=19.5</td>
<td>b=16.7</td>
<td>b=15.7</td>
</tr>
<tr>
<td><strong>B. BUFFALO MILK KHOA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>32.1</td>
<td>42.5</td>
<td>43.8</td>
</tr>
<tr>
<td>Fat</td>
<td>22.3</td>
<td>21.3</td>
<td>21.1</td>
</tr>
<tr>
<td>Fat FDM</td>
<td>32.9</td>
<td>37.5</td>
<td>37</td>
</tr>
<tr>
<td>Free Fat (% total fat)</td>
<td>54.5</td>
<td>20.3</td>
<td>12.1</td>
</tr>
<tr>
<td><strong>SENSORY QUALITY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flavour 'Score' (Max. 50)</td>
<td>48.6</td>
<td>48.6</td>
<td>40.6</td>
</tr>
<tr>
<td>Texture (Max. 35)</td>
<td>34.4</td>
<td>30.6</td>
<td>30.5</td>
</tr>
<tr>
<td>Comments</td>
<td>Typical flavour, grainy</td>
<td>Typical flavour, Slightly brittle</td>
<td>Lacks flavour, brittle</td>
</tr>
</tbody>
</table>

5.4 Use of RO processed milk for other dairy products

Whole milk and skim milk powders can be prepared using reverse osmosis as a first concentration step followed by either evaporation and spray drying or spray drying alone. Since milk is normally concentrated to 45-50% total solids before spray drying, RO cannot be used as a complete replacement of conventional evaporation. The reason for such a limitation of the process is that, with the current practice of RO, the permeation of water through the membrane practically ceases beyond 36-38% TS in case of whole milk and 27% TS in case of skim milk. Nevertheless, major savings in energy can be achieved by concentrating whole milk to about 30% TS and skim milk to 20-22% followed by concentrating to about 48% TS using multistage evaporator, and finally spray drying.

No appreciable differences in the properties viz., solubility, whey protein denaturation, powder morphology and bacterial population appeared between the
powders made from milk concentrated by RO process and those prepared by conventional process. The flavour and solubility of the spray powders made directly from RO concentrated milk were found to be superior than that of conventionally prepared powder. RO processed milk has also been successfully used in the manufacture of yoghurt, dahi, ice cream and several others.

6. REFERENCES


TECHNOLOGY OF WHEY POWDER

Dr. R.S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal-132 001

1. INTRODUCTION

Whey is the largest by-product of the dairy world. It is obtained during the manufacture of Paneer, Chhana, cheese, casein and Shrikhand. Maximum whey is produced by the cheese industry. Each Kilo of cheese gives rise to about 9 litres of whey. It has been estimated that about one million ton of whey is annually derived as a by-product which possesses about 70,000 tons of nutritious whey solids. Almost all the whey solids so obtained in India are wasted.

Nutritionally whey is a very important food item. It has been estimated that nearly 42-44% of the total solids in milk are to be found in whey. Whey contains about 6 per cent total solids of which protein and lactose constitute the major proportion, i.e. 12 and 70 per cent, respectively (Patel et al., 1991; Parekh, 1993). The whey protein has greater biological value (104) than the major milk protein casein (73). Whey is also rich in phosphorus and water soluble vitamins.

Whey is the strongest waste of any kind. One hundred kg of whey containing approximately 3.5 kg BOD and 6.8 kg COD, has the polluting strength equivalent to sewage produced by 45 people.

It is ironical to see that approximately one third of our population falls below poverty line and suffers from under nutrition (Jayaprakasha 1992). The protein and calorie intake in India is far below compared to developed countries. At this juncture, any possible source of food should be fully exploited to meet the demand and supply gap of nutrients. In this regard, whey solids have a promising role and appearing as a potential source. Recovery of whey solids offers an advantage, firstly, it solves the disposal problems and secondly it provides high quality whey solids for human use. Conservation of whey solids in the form of whey powder, whey protein concentrate, and lactose using membrane technology will certainly be a viable proposition. The powders owing to their high-nutritional and functional characteristics may find use in a wide range of food-formulations, such as bakery products, confectionaries, biscuits, beverages, gravies, soups, ice-cream, yoghurt, processed cheese and infant food (Kosikowski, 1979; Jayaprakasha 1992).

2. METHOD OF MANUFACTURE

The method of production of whey powder involves, clarification of whey, its partial concentration employing Reverse Osmosis process, followed by vacuum concentration, precrystallization of lactose and finally spray drying and packaging.
3. CLARIFICATION

When the whey is recovered from a cheese or casein manufacturing operation it is inevitable that low levels of 'curd' fines are present in the raw whey. These confer a serious risk of blocking heat exchanger channels or damaging UF or RO membranes. In addition, they may adversely affect the solubility properties and flavour of the end product (Jayaprakasha et al, 1995). Clarification of raw whey is usually achieved by either a combination of settling, screening and centrifugation alone depending on the size and level of fines.

4. SEPARATION

When whey is a sourced from a cheese-making operation there is usually a substantial content of fat present in it. For reasons of both economics and for flavour stability of the product, it is normal to strip the fat from whey. In practice, this is usually achieved using a self-discharging separator. More recently use of Microfiltration for the removal of residual fat from sweet cheese whey has found some application (Mathew, 1979; Merin and Tanny 1983). By using 0.8 micrometer porosity of membrane about 80% of the residual lipid can be removed.

5. HEAT TREATMENT OF WHEY

For sweet whey from either cheese or rennet casein manufacture, it is essential to pasteurize the whey immediately if optimum microbiological quality and storage stability is to be achieved. If the whey has to be cooled to 5°C. The time-temperature combination should be in the range of 72-75°C for 15-20 seconds for cow milk cheddar cheese whey and 80°C / 15 seconds for buffalo milk cheddar cheese whey (Jayaprakasha, 1992, Jayaprakasha et. al, 1995). The proper heat treatment will ensure reduction in viable counts, inactivate phosphatase and chymosin enzyme and to obtained maximum flux if partially concentrated employing RO process.

6. CONCENTRATION OF WHEY

The process of evaporation in the dairy industry has become of great significance in recent years, particularly in view of the cost of energy for both processing and transportation. In addition, the need to utilize whey through dehydration has led to major improvements in design for energy efficiency in evaporators, demanded by the low concentration of solids in the whey and the relatively low value of the product. For the manufacture of whey powder preconcentration of whey employing RO )Pepper and Orchard 1982) 22-22% TS is highly Economical. The removal of water, yielding 20-25% solids content, gives the opportunity to increase the capacity of existing evaporation equipment and the possibility to change the energy balance in a positive direction (Boer et al, 1975 Kjaergard and Oxchund 1988). This pre-concentration technique allows smaller cheese factories to increase the solids content in the whey and transport it to a centrally located factory for further processing. A simplified example of calculations which shows the rate at which a RO Plant concentrating 100,000 litre per day from 6-20% TS can pay for itself by reduction of transport costs.
It was also reported that the costs of concentrating 200,000 kgs whey/day is 20 percent lower by RO than by evaporation at concentration factor 2. However, at concentration factor 3, about 45% saving in total energy and 25 percent in overall costs (Sandfort, 1987). Moreover, the capital and energy cost including the one for preheating and cleaning process of a RO Plant would be less than 17 per cent of that used by conventional Evaporators. Also RO is reported to be 10 times more efficient in term of energy consumption than 5 stage evaporator or six time more efficient than 2 stage MVR process. Keeping in view of the benefits of RO process, this can be proposed as an Economical process for concentration of whey to recover valuable products as well as to minimize the disposal problem (Sandfort, 1987).

On other hand, evaporation by means of a falling film evaporator is most widely used for concentrating fluid dairy products. Whey and deproteinated whey may be concentrated to a level in the range of 50-52% solids as is most appropriate for the subsequent drying process.

Whey is generally concentrated to 40-60 percent TS depending on type of whey and quality of powder required. It should be noted that level of TS has a bearing on subsequent handling of the concentrate. When concentrating whey above 55 percent TS, there may be spontaneous lactose crystallization in the evaporator, leads to severe problems during further processing and drying (Westergaard, 1983). To avoid this phenomenon, a higher Evaporation temperature has to be used in the last stage of evaporators where lactose is most concentrated. When evaporation stages, numbered 1 to 7 in a seven-stage evaporator, were coupled in the sequence 1-2-3-4-7-6-5, the corresponding temperatures at the different stages were 68-65-61-57-39-45-50°C. After evaporation to a desired TS content, the concentrate is transported to double walled crystallization tanks which are equipped with slow running stirring devices.

7. CRYSTALLIZATION OF WHEY

To avoid the very undesirable caking properties of ordinary whey powder, it is of great industrial importance to get the major part of the lactose content in a crystalline form. The advantages of this lie both in energy savings and in improved powder properties. In the spray drier, it is possible to dry whey concentrate containing up to 60 percent solids, if the lactose content has been subjected to a crystallization degree of 85-90 percent. On the other hand, it is not possible to go higher in solids content than 42-45 percent, if the aim is to dry non-crystallized concentrate. Obviously this low degree of concentration has a very negative effect on the process economics compared to the process which involves crystallization. It is important to avoid spontaneous crystallization in the evaporator, by changing the flow pattern for the last evaporation stages, the output concentrate can thus be obtained at a sufficiently high temperature to avoid crystallization. Controlled crystallization can then be initiated by immediate flash cooling to about 30°C and subsequnt seeding. According to Westergaard (1983) the guidelines for crystallization are as follows: as soon as possible agitation should start and run at a speed that does not create foam in the concentrate. Immediately, fine grained alpha-lactose monohydrate at a level of about 1 kg per ton of concentrate should be added. The holding time under these conditions should be 3-4 hours cooling of the concentrate should then start, the rate being about 3°C/h until 10°C is reached.
Important factors which whey powder manufacturers should keep in mind for efficient and rich crystallization are:

i. As the crystallization rate is proportional to the existing surface area of the seeding crystals, it is important that the seeding material is very fine grained. The crystal size aimed at in the concentrate is 20-30 μm, and the biggest crystals should not exceed 50 μm.

ii. Sufficient agitation is imperative. This means that fresh, supersaturated solution is available continuously for interaction with crystal surface.

iii. A high viscosity of the concentrate - affected by the proteins and their time/temperature history - has a negative influence on crystallization. Therefore, every heat treatment from the very start of the manufacturing process should be taken into consideration.

iv. It is also necessary to control crystallization in order to create a maximum number of small crystals to give the largest total crystal surface and consequently, most rapid and efficient crystallization.

8. DRYING OF WHEY

The technique of drying and especially of spray drying is of great importance due to the fact that final powder quality concerning for instance nutritional and functional properties is determined to a great extent by the conditions of drying including pre and post-treatments of concentrates and powder, respectively (Jensen, 1987; Boersen, 1990).

8.1 Manufacture of hygroscopic whey powder

Lactoses in its amorphous alpha form is highly hygroscopic. Because of limited solubility, whey can be concentrated to only 42-45% total solids before being spray dried. Immediately, the dispersion of product in the drier may be by either high pressure nozzle or with a rotating disc atomizer. The inlet drying temperature is about 180°C and, in order to prevent the very hygroscopic powder being deposited, a high outlet air temperature is necessary (Kjaergaard and Oxlund 1988). This results in overall poor process economy and a product that has fine particles, is dirty, sticky, and highly hygroscopic.

8.2 Non-hygroscopic whey powder

After concentration and crystallization the whey solids should be at 50-55% and the lactose substantially in the alpha monohydrate form. Thus the material used to feed the drier results in improved economy since there is less water to be removed and better powder quality in respect of both larger particles size, higher bulk density and a greatly reduced propensity for caking through hygroscopicity (Kjaergaard and Oxlund 1988). The process parameters prior to the actual drying influence the quality of the product. To ensure the manufacture of high quality, non caking powder, the pre-heating conditions employed before evaporation are important. Pre-heating temperature must be 80°C and for approximately 20 seconds, holding time to ensure fast and abundant crystallization, good quality of the final product and to avoid excessive viscosity of the
concentrate. For non-hygroscopic whey powder an inlet temperature of about 185°C as recommended with an outlet temperature of about 85°C.

8.3 Spray drying operation

Spray drying can be divided into two processes, single effect drying and double effect drying. Double effect drying in contrast to single effect drying involves re-wetting of the spray powder containing 10-15 percent moisture, followed by a second drying stage in which the moisture content is reduced to below 5 per cent (Sienkiewicz and Riedel, 1990; Patel et al, 1991). In recent advances three stage drying techniques are also available. In one stage drying process (Boersen, 1990) the product is dried to its final moisture content in the spray drying chamber alone. The principle of two stage drying is a combination of spray drying as the first stage drying and fluid bed drying at the second stage. By this innovation it is possible to obtain agglomerated powder in a straight through process and also with advantage regarding product quality and drying economy in the manufacture of non-agglomerated products. Three stage drying or spray drying with integral fluid bed is an extension of the two stage concept by transferring the second drying stage into the spray drying chamber and having the final drying conducted in the third stage located outside the drying chamber.

9. CHEMICAL COMPOSITION OF WHEY POWDER

Composition of whey powder varies depending on the type of whey from which it has come, pretreatment given to the whey, and the various processing steps followed in the production.

Analysis of commercially produced sweet and acid type dry whey revealed the values for lactose, total protein, NPN, total ash and fat for sweet and acid type whey powders were 69.4, and 63.4 per cent, 13.0 and 11.7 per cent, 0.5 and 0.58 per cent, 8.3 and 10.6 per cent and 1.03 and 0.48 per cent, respectively. The moisture content varied from 3.7 to 6.0 percent. (Sienkiewicz and Fiedel 1990)

10. STORAGE OF WHEY POWDER

Non enzymatic browning via Maillard reaction is one of the important modes of deterioration in whey powder, which limit shelf life. Whey powders contain relatively high concentration of lactose and protein. In the presence of moisture these components readily participate in the Maillard reaction. This interaction may result in a decrease in protein quality which is accompanied or followed by undesirable color changes.

Rennet whey powder can be kept for a maximum of 60 to 80 days at 20°C if intended for use in the food stuffs industry. If whey powder is to be kept in an acceptable condition over a 3 month period or longer, the storage should be at 15 to 20°C with 10 to 15 percent relative humidity and under air tight conditions (SienKiewicz and Riedel, 1990; Jayaprakash, 1992).

The scientists of Dairy Technology Division (Dr. R.S. Patel and Dr. H.M. Jayaprakasha) of NDRI Karnal, in collaboration with German Scientists Prof. E.Renner
have developed a technology for conversion of whey into whey powder. The salient features of the investigation are as follows:

11. PRODUCTION OF WHEY POWDER

- Processing of whey by RO at 50°C with an operational pressure of 35 bar was found to be economical. With respect to cow milk cheddar cheese whey (CW) and buffalo milk cheddar whey (BW), clarification and preheating to 80°C / 15 sec at 6.3 and 7.2 pH respectively prior to RO resulted in maximum flux. Clarification of paneer whey (PW) was not beneficial but preheating to 80°C / 15 sec at 7.2 pH resulted in significantly higher flux. At these treatments, the fouling and deposit formation were kept to minimum.

- Concentration of PW, CW and BW by RO followed by vacuum concentration to 50 percent TS resulted in savings of 55.73, 67.07 and 67.68 per cent energy respectively compared to conventional evaporation alone.

- Precrystallization of PW concentrate (50% TS) with 0.03 percent - α -lactose monohydrate for 4 h at 30°C yielded maximum crystallization (PW, 79%; CW, 75% and BW 73%) (Jayaprakasha et al 1995)

- The whey powders manufactured in our investigation compared well with those of commercial whey powders with respect to physical and functional properties. The composition of cheese whey powders with respect to protein, lactose and ash varied from 12.51 to 14.33, 72.99 to 75.49 and 7.34 to 8.01 per cent respectively. Whereas the lysine content varied from 7.25 to 7.70 g / 100 g protein.

- The chemical changes in whey powders during storage were minimum at 20°C. Polycrystalline was observed to be as good as metallocrystal polymer for storage of whey powder. The losses of lysine after 6 months of storage varied from 8 to 28 percent depending on storage temperature.

12. REFERENCES

MICROFILTRATION AND ITS APPLICATIONS IN DAIRY INDUSTRY

D. K. Sharma
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

Microfiltration is essentially a method of separating suspended particles from dissolved substances in feed stream such as Bacteria, (0.5-5 μm) DNA, viruses (<1000 Å), Blood cells, starch (10 μm), Pollen (100 μm). Microfiltration is also a pressure driven (0.1-8 bars) separation process using symmetrical or asymmetrical membranes of pore sizes in the range of 0.1 to 10 μm. However, ultrafiltration membranes are little more dense and used to separate particles or molecules in the range of 1000 to 100,000 molecules range or 10Å to 100Å.

The first microfiltration membrane filter based on Zsigmondy Technology was manufactured by Membran-Filtergesellschaft Sartorius Werks in Göttingen, Germany. The firm began selling mostly for laboratory research in 1929. The roots of the international microfiltration industry really took hold, when there was a need to rapidly analyze for bacteria in the water supplies of bombed-out German cities immediately following World War II. At that time the U.S. Army also had an interest in the use of these membranes for detection of biological warfare agents. This interest led to a contract between the Army Chemical Corps and Professor Alexander Goethe at the California Institute of Technology, which ultimately led to the establishment of the Millipore Corp in the United States.

Initially, the primary use of microfiltration membranes was in the bacteriological analysis of water. The membrane filter was used to retain bacteria on surface and by supplying nutrients from underneath filter, the bacterial colonies can be grown in matter of hours and easily counted under the microscope. It is an approved method of analysis of water and wastewater as well as the Public Health Service Drinking Water standard in U.S.

Until 1963, microfilters were predominately nitrocellulose, or a mixture of cellulose esters. The need for improved chemical resistance and heat stability of membrane prompted investigations of new materials and method of fabrication (Cheryan, 1986; and Porter, 1986). Until then the main uses of microfilters have been water purification and sterilization, and microbiological and related applications such as direct epifluorescent filter techniques (DEFT). In food industry later, they are mainly used for water, and beverage sterilization. The industrial units are stack-plate filters and cartridges servicing as filter, all of which have been operating as depth or dead-ended filters (Bertera et al., 1984).
2. TANGENTIAL OR CROSS FLOW MICROFILTRATION (MF)

For improving the performance of dead-ended filter or depth filters, the new crossflow filtration process came in existence for industrial applications. It is a pressure driven membrane process, similar to ultrafiltration (UF). MF could be used for coarse filtration of particulate and bacteria as well as to fine separation of soluble proteins and small molecular solutes from water. MF processes usually operate at pressures of 0.1-8 bars which at the lower range are somewhat lower than UF.

3. SEPARATION DYNAMICS OF MICROFILTRATION

MF membranes do not merely operate on molecular weight rejections as do UF and RO membranes. Since MF deals with particles and colloids even when eliminating the limiting fouling phenomena, separation will still be governed by other factors rather than pure pore size. Most molecules greater than pore size, will be retained as in UF, but transmission of species smaller than the pores will be attributed to various factors. These factors include particle stearic configuration and charges, hydrodynamic friction with other species and membrane surface, surface-particles, pore wall-particle and particle-particle interactions and pressure drop across the membrane and module.

Since in the dairy industry we are not dealing with a uniform size ideal feed stream, the above mentioned factors are of tremendous importance. More over dairy particles are also of different size and shape which ultimately enhanced the affect of above factor manifold in MF process. As evident charges play a major role in respect to interactions between particles, colloids and metal ions and thus, any pH, temperature, pressure changes etc. will result in change of membrane performance with time.

4. CROSS FLOW MICROFILTRATION (CFMF) MEMBRANES

At present, microfilters are commercially available from several manufacturers in different configuration (Tubular, plate and frame). The most suitable configurations for microfiltration is 'tubular', it can handle viscous liquids because it can achieve high velocities on membrane surface. Flat sheet membranes could also be used in any existing plate- and - frame or flat-sheet tangential flow membrane units. In order to obtain an acceptable MF performance it is necessary to study and assess the right membrane characteristics with respect to sharp pore diameter, process variables (temp., pressure, velocity) and special treatments of the feed streams.

5. APPLICATIONS IN DAIRY INDUSTRY

CFMF is an adequate tool for use in the dairy industry for several purposes:-

a) Separation of bacteria from whole or defatted milk
b) Separation of fat from whole milk and casein micelles from soluble proteins.

c) Clarification and defatting the cheese whey.
d) Phosphocascinate separation.

6. MICROFILTRATION OF WHEY

The first report by Tanny et al. (1982) dealt with pre-treatment of whey for defatting and casein fines removal from sweet whey and for cheese brine clarification. The protein retention from whey in CFMF using 1.2 μm membranes was reported to be 5-6% (Merin et al., 1983). Globular fat was totally removed from permeate stream while bacteria was reduced by 2-3 orders of magnitude. It was observed that microfiltered whey had 25-30% higher UF fluxes compared to centrifuge-clarified whey.

Inorganic carbon ZrO₂ MF membranes along with some polymeric membranes rejected about 15-20% of the proteins and lowered bacteria counts by 5 orders of magnitude (Piot et al., 1984).

Hanemaajier (1985) reported the use of CFMF for pre-treatment of whey for manufacture of WPC. The studies conclude that all the modules were not removing fat to a desired level, and suggested a combined MF/UF process for WPC manufacture after initial concentration of the feed whey by RO or evaporation. In batch concentration of whey with a total solids content of 25% up to a volume reduction of 80%, they reported possible fat reduction factor of 20-60, using CFMF. Owing to membrane fouling, fluxes were low (25-53 l/h m²) depending on membrane type.

It is now commercially possible to remove residual fat (aggregate of phospholipoproteins (PLP) from whey using M-14 carbon-ZrO₂ membrane (0.14 μm pore dia) with flow velocities of 6 m/sec giving a flux of crystal clear whey at the rate of 60 litres/h m². This pretreatment increased UF-fluxes to 1.8 times while making high quality WPC. The condition of CFMF for whey defatting have been: temp. 50.ºC, transmembrane pressure 0.9 bars, velocity 6 m/sec.

7. MICROFILTRATION OF MILK

Alfa-Laval Company way back in 1975 patented a process for defatting milk with polymeric membranes. The patent registrations covered were: slow flow velocities (<0.5 m/s), 0.2 kg/cm² pressure drop.

It appears from the relative diameter of some milk constituents (Table 1) that with skimmed milk, it is possible to separate bacteria from the milk components, whereas, with whole milk, most of the fat is removed with bacteria (Muir and Bank, 1985).

The first pilot studies on MF of whole milk were reported in 1987 (Piot et al., 1987). It was shown that MF process using an inorganic alumina membrane of 4 mm ID and 1.8 μm pore size could skim 98% of the fat and reduce bacterial counts by 2 orders of magnitude with no apparent retention of proteins.

Semi-Industrial trials were carried out using alumina membranes of 1.4 μm pore size with co-current circulation of permeate. The units were operated at constant fluxes of upto 700 l/h m² for over 6 hrs with 0.1 bar increase in TP for VCR 10 (Malmberg
and Holm, 1988). It was shown that 99.7% of bacteria could be removed from skimmed milk with fluxes over 640 l/hr m\(^2\). Removal of Clostridia spores using MF was 10 times better compared to bactofugation, regardless of initial count. Removal of \textit{Bacillus cereus} was also as effective with the use of CFMF. Based on these initial studies, Alfa-Laval has patented a process called 'Bacto Catch' for removing bacteria from skim milk using Alumina membrane of 1.4 \(\mu\)m. With skim milk at 50\(^\circ\)C the operational flux have been 500 litres/hr m\(^2\) at a concentration of 1:10. The bacterial count was reduced to 99.91%. The retentate (having bacteria and some milk solids) was heat treated (130\(^\circ\)C) and recombined with filtrate and whole lot was pasteurized. The keeping quality of milk is enhanced further for 3-4 days.

8. PHOSPHOCASEINATE SEPARATION

Microfiltration (carbon-\(\text{ZrO}_2\)) membrane (0.2 \(\mu\)m pore dia) have been utilized for concentrating phosphocaseinate complex in native state. In the process, the skim milk is pasteurized at 72\(^\circ\)C for 15 sec and microfiltered at low transmembrane pressure and 6 m/sec tangential flow velocity. The resulting permeate is an 'ideal' whey without fat, bacteria, rennet and glycomacropeptide (Maubois, 1988). The retentate is the native phosphocaseinate which could be further purified by diafiltration.

9. CONCLUSION

In order to assist the implementation of CFMF in dairy industry, few points must be fulfilled. Fouling must be limited by thinning of the concentration polarization or cake layer by high tangential flow rates. It will necessitate the manufacture of systems to overcome the high pressure drops. Adsorption of feed components to the membrane should be kept to a minimum by using appropriate membrane materials and/or special pre-treatment of their surface. Proper selection of membrane pore size and pore size distribution to fit particle size and the use of pumps which do not alter particle size due to shear forces could result in less fouling and better selectivity. In years, to come CFMF shall be one of the unit operation in our dairy plants.

Table 1: Relative Diameter of Milk Constituents

<table>
<thead>
<tr>
<th>Components</th>
<th>Size (nm)</th>
</tr>
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<tbody>
<tr>
<td>Water</td>
<td>0.3</td>
</tr>
<tr>
<td>(\text{Cl}^-, \text{Ca}^{2+})</td>
<td>0.4</td>
</tr>
<tr>
<td>Lactose</td>
<td>0.8</td>
</tr>
<tr>
<td>Whey Protein</td>
<td>3 - 5</td>
</tr>
<tr>
<td>Casein micelles</td>
<td>32 - 300</td>
</tr>
<tr>
<td>Fat globules</td>
<td>100 - 2000</td>
</tr>
<tr>
<td>Bacteria</td>
<td>&gt; 200</td>
</tr>
</tbody>
</table>
10. REFERENCES

USE OF REVERSE OSMOSIS IN KHEER MAKING

Dr. G. S. Rajorhia
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

A variety of cereal based milk products are prepared in Indian households. The nutritional significance of these products has been investigated and documented in the literature with reference to growth and longevity. The cereal based milk products like Kheer, Payasam, Kunda, Seviyan (Vermicelli) and Besan Burfi are quite popular in the different regions of India. Rice pudding, rice cream, Porridge and similar products can be found with different brand names on the market shelves in Asian countries, Australia, New Zealand, Germany and other European countries. All these products primarily involve heating processes to achieve varying degree of milk solids concentration and gelatinization of cereals. Invariably in most cases, sugar, dry nuts and flavours are added to enhance the taste and shelf life of the product. Kheer tops the list among cereal based milk products in the world.

2. CURRENT MANUFACTURING PRACTICE

Kheer is prepared by cooking of rice in milk with continuous stirring and seraping to hasten the process of evaporation and to achieve certain degree of concentration. Rice and cane sugar are added after 3-5 min. of boiling. It usually takes 30-35 min. to prepare a small lot of 2-3 Kg. kheer in a kitchen. The viscosity of kheer varies depending upon the proportions of rice and milk, degree of concentration, amount of sugar and other ingredients added and cooling regimes. The shelf life of the product is limited to about one day at room temperature and 2-3 days in the refrigerator.

In one laboratory experiment, kheer was prepared from standardized milk having 4% fat with 2.5% rice and 5% sugar. The average percent composition of 20 samples of kheer was: moisture-67, fat-7.8, protein-6.3, lactose-8.5, sucrose-9.0, and total ash-1.4. The shelf life of the can sterilized samples was 3-4 days. Addition of nisaplin enhanced the shelf life to 8-10 days at 37°C. This experiment proved that a simple scaling up of the household level technology may not be the right approach to commercial production of kheer. Systematic work was, therefore, undertaken for critically examining the various unit operations adaptable to industrial production of kheer. Reverse osmosis seemed to be an attractive method of concentration without any appreciable damage to nutritional properties which are otherwise caused by conventional heating.

3. OBJECTIVES OF RESEARCH

The constraints and limitations of the existing traditional technology would not permit the organized dairy industry to scale up and mechanize the process of kheer...
making in a continuous mode. The modern dairy industry is seeking innovative approaches to product diversification. Reverse osmosis as a process of selective concentration offers scope for mechanizing kheer production. The objectives of the investigation were centred around RO process for formulation of the product mix using various levels of milk solids concentration, optimization of processing conditions to improve heat stability and extension of shelf life by employing batch and UHT methods of sterilization.

4. USE OF RO CONCENTRATED MILK IN KHEER MAKING

A. The following studies were conducted to formulate the product:

a) Quality of milk
b) Milk solids concentration (17.0, 19.5, 22% T.S.)
c) Variety of rice and rate of addition, grain size, effect of washing of rice on kheer quality.
d) Use of hydrocolloids as thickeners, considerations in the selection of guar gum.
e) Appropriate sugar levels (8, 10, 12% of the mix)
f) Effect of homogenization of RO milk on kheer quality.
g) Addition of flavourings.

B. Improvements in the heat stability of RO concentrated milk for sterilization:

a) Sterilization time and heat stability.
b) Role of milk solids concentration and heat stability.
c) Influence of pH on heat stability of RO concentrated milk during batch sterilization.
d) Improvements in heat stability using phosphatic stabilizers.

C. Microbiological and shelf life studies at 30°C and 4°C.

The results of the above experiment will be presented and discussed.

5. MARKETING POTENTIAL FOR KHEER

In order to evaluate the prospects of marketing of kheer manufactured with the help of newly developed integrated system, selected test market trials were conducted to study the consumer awareness, product quality and safety. The response was very encouraging. Scope exists for establishing national marketing network for kheer. Developing countries of Asia and Africa also offer tremendous marketing opportunities.
LACTOSE MANUFACTURE USING MEMBRANE TECHNOLOGY

Dr. Vijay Kumar Gupta
Dairy Technology Division, NDRI (ICAR), Karnal-132 001

1. INTRODUCTION

Lactose is the major carbohydrate in the milk of most animals. Lactose in its pure form is a white, water soluble crystalline powder of moderately sweet taste with no odour. The pharmaceutical and foodstuffs industries represent the permanent market for lactose which serve, above all, for application in tablet production, as an additive in culture media and for the production of baby food, pastries and confectioneries. The exact world-wide production of lactose can not be accurately assessed as not even the Food and Agricultural Organisation has statistical data. As a rough estimate, the quantity of lactose produced on a world-wide scale amounts to some 50 lakh MT per annum.

Lactose can be isolated on a commercial scale from whole whey or from deproteinized whey. Recently the use of membrane methods for the concentration and fractionation of milk in the dairy industry is being expanded. The protein and mineral contents of the whey are the limiting factors for the crystallisation of lactose, and this is the reason why the permeate obtained by ultrafiltration of whey is preferred as the starting material in the production of lactose. Sometimes minerals are partly removed prior to lactose production using electrodialysis, ion exchange or nanofiltration. Further for partial concentration of whey or UF permeate, reverse osmosis is being employed.

The most common form of commercial lactose is α-hydrate, very little lactose is in the form of β-anhydride. Lactose crystallises as α-hydrate from saturated solution at temperature below 93.5°C. The crystals contain one molecule of water per molecule of lactose. The β-anhydride which contains no crystalline water, is formed when the crystallisation takes place at temp. higher than 93.5°C. The crystallisation of lactose from saturated solution in the α-form which is less soluble. Crystalline lactose isolated from whey or from UF whey permeate is in the form of the α-hydrate or β-anhydride or a mixture of both forms.

2. CLARIFICATION OF WHEY BY MICROfiltrATION

Microfiltration is a pressure-driven membrane separation process using porous membranes with cut off pore size in the region of 10^-6 m allowing passage of proteins. Microfiltration is done at 55°C and can be used to remove large particles, casein fines, micro-organisms or microbial spores, fat globules, somatic cells, phospholipoproteins etc. from whey.
3. LACTOSE MANUFACTURE FROM UF PERMEATE

Table 1 gives the composition of UF permeate streams with Cheddar cheese and casein whey. UF permeate gives relatively higher yield and purity of lactose than whey. At present, nearly 12% of the total whey utilised is processed by ultrafiltration. The general manufacturing process of lactose from whey involves deproteinization, concentration by evaporation, crystallisation, separation, refining, drying and milling. However, direct application of this technology to UF permeate is not straightforward.

Table 1. Chemical composition of UF permeate stream from Cheddar cheese and casein whey

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Cheddar cheese</th>
<th>Casein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (%)</td>
<td>6.40</td>
<td>5.9</td>
</tr>
<tr>
<td>Lactose (%)</td>
<td>5.80</td>
<td>4.6</td>
</tr>
<tr>
<td>Total N (%)</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>NPN (%)</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0.54</td>
<td>0.74</td>
</tr>
</tbody>
</table>

3.1. Demineralisation

The removal of minerals from whey or UF permeate is beneficial as it improves heat transfer during heat evaporation by reducing the formation of deposits of calcium. Also the yield of the product is increased, since the crystallisation of lactose is not hindered by salt concentration. UF permeate is virtually saturated with calcium. This is particularly true of acid whey permeate. Concentration by evaporation causes precipitation of calcium salts and can result in rapid fouling or scaling of heat exchanger surfaces. It is generally accepted that UF permeate must be pre-treated either prior to or during evaporation. Suitable process includes exchange of calcium for sodium ions by ion exchange resins or demineralisation by electrodialysis and/or ion exchange processes. Other suggested pretreatments include reducing pH to eliminate formation of insoluble salts and addition of food grade calcium chelating agents (e.g., sodium hexametaphosphate) to form insoluble complexes that may be removed prior to crystallisation. Hobman (1984) reported on processes to reduce calcium salt levels by up to 80% by treating with alkali and heat. In Pilot scale trials to ascertain the suitability of pretreatment process for the manufacture of crystalline lactose from UF permeate, it was observed that removal of approx. 50% calcium was sufficient to avoid difficulties during evaporation.

3.2. Partial demineralisation and concentration by nanofiltration

Electrodialysis and ion-exchange processes are effective but have limited use because of high capital cost, high running cost and high level of effluents. Recently introduced technology known as ultra-osmosis, nanofiltration or loose reverse osmosis uses membranes which are selectively permeable to water and minerals, but substantially retentive to lactose. Nanofiltration performs two functions simultaneously i.e. it partially demineralises a solution, while concentrating the bulk of the proteins, fat
and lactose contents. It can be used for the concentration and partial demineralisation of whole whey up to 28% of dry matter and also for concentration of the UF permeate. Demineralisation of cheese whey by nanofiltration shows 20-45% overall demineralisation while more than 90-95% of non-ionic species like lactose are retained. A 2-5% loss of lactose can be expected in a typical whey nanofiltration process.

3.3. Concentration

The concentration of whey permeate to a particular total solids level is very critical because, a higher total solids concentrate would be too viscous, while a lower total solids concentrate would result in lesser lactose crystallisation. The absence of proteins in UF permeate solution causes reduction in viscosity and thereby permits concentration to higher total solids. The permeate is concentrated to a solid content of 60% or more (upto 70%). This is performed either by a pre-concentration through reverse osmosis, followed by evaporation or merely by evaporation. Reverse osmosis has the potential for removing a major portion of the water from whey or permeate more economically than the evaporator process, but it has the limitation that, for required concentration, it has to be followed by evaporation. Evaporation is carried out in multi effect evaporators for economic reasons. For a higher level of concentration of whey, a combination of reverse osmosis and evaporation is the most energetically favourable way. The greatest problem in the concentration of whey by reverse osmosis is the membrane fouling and concentration polarisation resulting in reduced permeation rates. A pre-treatment of the whey as known from ultrafiltration has a negative effect when concentrated through reverse osmosis. This implies that the mineral constituents, in quantity and form, are more important for the flux of reverse osmosis units than is the protein. The most effective pre-treatment for HCl-whey is demineralisation by means of electrodialysis or by ion-exchange. Unspecified, highly active proteases are used during the cleaning of reverse osmosis plants. The concentration process must be conducted in such a way that no lactose crystallisation takes place in evaporator and piping. This is done by keeping the temperature and concentration within metastable area.

3.4. Crystallisation

Crystallisation is initiated in the hot concentrated whey or UF permeate. This is a complex process during which lactose molecules diffuse to the crystal surface and simultaneously release and transfer the heat of crystallisation from the crystal to the liquid. The purpose of crystallisation is to secure the formation of crystals that can be separated from the mother liquor. Cooling of the lactose syrup to a temperature below saturation temperature is necessary for crystallisation of lactose. During crystallisation, β-lactose is converted into α-lactose which is crystallised out. The crystallisation rate depends on available crystal surface for growth, purity of the solution, degree of supersaturation, temperature, viscosity and agitation. The increase in temperature, generally increases the growth rate of crystals. Using UF permeate as the starting material would have the associated advantage of shorter crystallisation time. For easy recovery of lactose crystals, their size must be sufficiently large to ensure quick settling of crystals. Easy recovery is obtained with an average size of 0.2 mm. The number of crystals and their average size can be controlled by seeding the concentrate with a known number of very fine lactose crystals. The seed crystals must be added in the
form of fine particles of α-lactose monohydrate at the rate of 1 kg per ton of concentrate. The cooling of the concentrate should be slow. The entire crystallisation process lasts between 15-24 hours under constant slow agitation. Automatic systems in lactose crystallisation tanks are available to regulate temperature within ±0.5°C. The system can be supplied pre-programmed since random access memory has a battery buffer to prevent loss of data in case of power failure.

3.5. Harvesting of lactose crystals

Recovery of lactose crystals can be carried out batchwise in basket centrifuges, which have the advantage of permitting complicated wash cycles. However, continuous decanters equipped with a screw conveyor for crystal discharge are used more frequently. The liquid phase overflows and consequently a liquid level is formed. The solid outlet ports are situated higher, and crystal mass is discharged with a relatively low moisture content. The screw conveyor runs at a slightly different speed as compared to drum and it permits the transport of heavy phase. The crystals from decanter are fed into a second decanter in order to improve washing and removal of mother liquor. The overflow of liquid phase from decanter depending upon its purity, can be recondensed and recrystallised. The washed crystals recovered in decanter have a moisture content of approximately 10% and can be dried directly.

A specially designed centrifuge gives a high degree of separation of lactose crystals from condensed cheese whey. Crystals of 40 μm can be recovered with final moisture content of 1.5-2.5%. Another designed centrifuge proved capable of continuously separating crystalline lactose with 2.5-2.9% moisture from concentrated whey at the rate of 250-300 kg/hr.

Table 2. Lactose Commercial - Specifications (IS 1000:1989)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Specifications</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Lactose (on dry basis), % by mass, min.</td>
<td>99</td>
</tr>
<tr>
<td>2.</td>
<td>Moisture % by mass, Max.</td>
<td>5.5</td>
</tr>
<tr>
<td>a) for Lactose, monohydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) for Lactose, Anhydrous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Sulphated Ash (on dry basis), % by mass, Max.</td>
<td>0.2</td>
</tr>
<tr>
<td>4.</td>
<td>pH (of 10% solution)</td>
<td>4.0-6.5</td>
</tr>
<tr>
<td>5.</td>
<td>Sp. rotation</td>
<td>52.0-52.6</td>
</tr>
<tr>
<td>6.</td>
<td>Nitrogen, % by mass, Max.</td>
<td>0.05</td>
</tr>
<tr>
<td>7.</td>
<td>Arsenic (AS) Mg/Kg, Max.</td>
<td>1</td>
</tr>
<tr>
<td>8.</td>
<td>Lead (Pb) mg/1g, Max.</td>
<td>2</td>
</tr>
<tr>
<td>9.</td>
<td>E. coli, per 0.1 g</td>
<td>Absent</td>
</tr>
<tr>
<td>10.</td>
<td>Salmonella, per 0.1 g</td>
<td>Absent</td>
</tr>
</tbody>
</table>
3.6. Refining of lactose

For high degree of purity, as in pharmaceutical grades, refining of lactose is done by subjecting crude lactose to treatment for removing colour, residual protein and salts followed by recrystallisation. Less refining is required for lactose prepared from permeate than that made from whey. Crude lactose is dissolved in hot water to a 50-60% concentration depending on its purity. About 1% of decolorizing paste consisting of 3 parts bone black, 1 part activated carbon and 1 part 36% HCl is added. Quick dissolution requires heating to 105°C. Acidity is reduced by addition of Ca(OH)₂. Carbon absorb colour and probably removes other impurities to some degree. HCl is added to assist the action of carbon, to solubilize salts and to aid in removal of protein. Lime is used to adjust the reaction to that most favourable for the precipitation of protein, and probably aids by combining with the protein to some extent. The liquid is boiled and filtered with the assistance of filter aid to remove carbon and precipitating impurities at high temperature to avoid premature crystallisation. The resultant clear solution is further evaporated to 70% TS and introduced into crystallising tanks. The crystals are gradually cooled to approximately 20°C in about 6 hours. After cooling, crystals are separated.

3.7. Drying of lactose

Edible lactose is normally dried to 0.5% moisture content and pharmaceutical lactose to 0.1% moisture content. The drying process is limited to a product temperature of 93°C, otherwise lactose will be crystallised into β-lactose anhydride at temperature above 93.5°C. Another important factor is the drying time. Flash drying can easily result in the formation of a thin layer of amorphous lactose on α-hydrate crystals, resulting in the risk of lumps formation in the bagged lactose afterwards. A fluidized bed drier with a maximum product temperature of 92°C/15-20 min would give good results. Pneumatic transport of lactose from the drier must be carried out by means of dry air at about 30°C. It gives gentle product cooling.

3.8. Milling and bagging of lactose

Dried lactose is milled and sifted through 100-200 mesh sieve and hermetically sealed in moisture proof bags.

3.9. Grades of lactose

The international trade recognises several commercial forms of lactose:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Grade</th>
<th>Lactose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Technical lactose</td>
<td>90-92</td>
</tr>
<tr>
<td>2</td>
<td>Crude lactose</td>
<td>95-99</td>
</tr>
<tr>
<td>3</td>
<td>Food grade lactose</td>
<td>98-99</td>
</tr>
<tr>
<td>4</td>
<td>Pharmaceutical lactose</td>
<td>99.5-99.9</td>
</tr>
</tbody>
</table>
4. REFERENCES


APPLICATION OF ULTRAFILTRATION IN CHEESE MAKING

Dr. S.K. Kanawjia
Dairy Technology Division, NDRI (ICAR), Karnal-132 001.

1. INTRODUCTION

Ultrafiltration is now considered to be a need based processing operation in dairy industry. The two largest applications are preconcentration of milk for cheese manufacture and fractionation of cheese whey. Traditional cheese making has been defined as a "fractionation process by which fat and casein are concentrated in the curd, while lactose, soluble proteins, minerals, and vitamins are lost in the whey fraction". UF was first proposed for use in cheese making in 1969 by Maubois, Macquot, and Vassal (1969). The major use in the manufacture of soft cheeses, defined as those containing more than 45% moisture. Typical examples are Mozzarella, Camembert, Brin, and Cottage cheese. These continuous effort has been made to manufacture hard cheese using UF milk. An appreciation of the application of ultrafiltration to making the various types of cheese is presented in Table 1 which compares the solids contents of UF concentrate according to concentration factors with the solids contents of the cheeses.

2. ADVANTAGES OF CHEESE MAKING BY UF

(i) It increases the yield of cheese upto 10-30%. This is due to entrapment of whey proteins and possibly some bound water associated with the whey proteins.

(ii) It reduces the energy requirement, because concentration of milk components is carried out using membrane which consumes less energy than the traditional long-held heating and cooking steps.

(iii) The requirement of enzyme is considerably reduced for a given amount of milk processed or cheese produced.

(iv) Whey disposal problems are reduced because there is less whey drainage, depending on the extent of UF concentration. The UF permeate generated is relatively sweet, clear contains no proteins but a small amount of non-protein nitrogen, is high in fermentable carbohydrates and thus can be treated or disposed off easier than acid whey.

(v) It reduces the space requirements due to the smaller volume of milk handled per unit weight of cheese. This leads to better utilisation of existing cheese vats.

(vi) Mechanisation and automation in cheese making is possible.
Table 1. Ultrafiltration for cheese making: the solids contents of varieties of cheese and of the milk concentrates at concentration factors 1-9.

<table>
<thead>
<tr>
<th>Variety</th>
<th>Cheese Solids content (%)</th>
<th>U.F. Concentrate Solids content (%)</th>
<th>Conc. factor</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ymer</td>
<td>15</td>
<td>12.5</td>
<td>1</td>
<td>87.5</td>
</tr>
<tr>
<td>Cottage</td>
<td>21</td>
<td>18.8</td>
<td>2</td>
<td>81.2</td>
</tr>
<tr>
<td>Quarg</td>
<td>21</td>
<td>18.8</td>
<td>2</td>
<td>81.2</td>
</tr>
<tr>
<td>Ricotta</td>
<td>28</td>
<td>25.1</td>
<td>3</td>
<td>74.9</td>
</tr>
<tr>
<td>Feta</td>
<td>40</td>
<td>25.1</td>
<td>3</td>
<td>74.9</td>
</tr>
<tr>
<td>Petit Suisse</td>
<td>45</td>
<td>31.4</td>
<td>4</td>
<td>68.6</td>
</tr>
<tr>
<td>Mozzarella</td>
<td>46</td>
<td>31.4</td>
<td>4</td>
<td>68.6</td>
</tr>
<tr>
<td>Camembert</td>
<td>47</td>
<td>37.5</td>
<td>5</td>
<td>62.5</td>
</tr>
<tr>
<td>Coulommier</td>
<td>47</td>
<td>37.5</td>
<td>5</td>
<td>62.5</td>
</tr>
<tr>
<td>Queso Blanco</td>
<td>49</td>
<td>33.8</td>
<td>6</td>
<td>56.2</td>
</tr>
<tr>
<td>Cream cheese</td>
<td>50</td>
<td>50.1</td>
<td>7</td>
<td>49.9</td>
</tr>
<tr>
<td>Danish Blue</td>
<td>57</td>
<td>50.1</td>
<td>7</td>
<td>49.9</td>
</tr>
<tr>
<td>Edam</td>
<td>58</td>
<td>50.1</td>
<td>7</td>
<td>49.9</td>
</tr>
<tr>
<td>Herve</td>
<td>62</td>
<td>62.9</td>
<td>9</td>
<td>37.1</td>
</tr>
</tbody>
</table>

3. TECHNICAL PROBLEMS IN CHEESE MAKING FROM ULTRAFILTERED MILK:

The conversion of retentate into cheese presents new manufacturing problems and major technological difficulties are known to exist when making some types of UF cheese. These limitations need to be recognised if the process is to be assessed objectively.

3.1 Viscosity of retentate

The viscosity of retentate increases markedly when the protein content exceeds 14%. Hence milk concentrated 5-fold or more is comparatively viscous. It is therefore, difficult to mix rennet and starter uniformly with such milk and consequently coagulation and starter growth may be uneven. As a result, the pH throughout the retentate may vary and problems with cheese texture may occur. In addition, because retentates have a high viscosity they do not cool quickly and rapid growth of microbial contaminants can therefore occur. Another problem associated with the high viscosity
is that any air bubbles in the retentate are not released quickly and become incorporated into the product, giving a spongy texture.

3.2. Starter activity

A basic difference between traditional and UF cheese making is the higher buffering capacity per unit volume of retentate. Relatively large amounts of lactic acid must be produced to give the required pH changes in the concentrated milks. The ability of lactic cultures to develop acid in retentates varies considerably and only highly active starters must be used. Failure to reduce the pH increases the risk of growth of undesirable bacteria. Some starters grow to large numbers in retentates, resulting in high concentration of bacterial enzymes and a greater degree of proteolysis in certain types of UF-cheese.

3.3. Coagulation of concentrated milks

Gel formation usually occurs in UF concentrates when only a relatively small fraction of the micellar K-casein has been hydrolysed. As the concentration of milk increases, this fraction decreases. Micelles that are not sufficiently modified at the point of coagulation are gradually hydrolysed as cheese making proceeds and become incorporated into the coagulum network structure. Gel prepared from retentates become progressively coarser as the concentration factor of the milk increases. When these gels are converted into UF-Cheddar cheese, the coarse protein network is maintained and the differences between traditional and UF curds can be observed throughout cheese making. The ability of UF curd to retain fat and moisture is said to decrease as the curd becomes coarser. Electron microscopic studies indicate that UF curd has a coarser protein network and differs in basic structure from a conventional curd. The more fragile nature of UF curd has been attributed to this difference in structure. Manufacturing problems due to the fragility of UF curd are accentuated by the fact that there is less whey to cushion it from physical damage and prevent the material from aggregating.

4. MANUFACTURE OF CHEESES

4.1 Camembert

For making Camembert type cheese, initially pasteurized skim milk was concentrated about 5-fold by ultrafiltration. Cream was added to bring the composition of this pre-cheese near to that of the desired product. Then followed lactic acid bacteria, rennet and salt and the liquid was poured directly into the cheese moulds. Within about 10 minutes the curd had formed from which subsequently only a little whey drained. The cheese was cured as a slightly higher temperature than usual, with a yield of 16% above that obtained by the traditional method.

Later, fat standardized milk was used, pre-acidified to pH 6.0-6.2 with 0.8% starter. This was concentrated 5-fold by UF, acidified further to pH 5.5 to 5.7 and then made into cheese. A 20% increase in yield was claimed with improved uniformity in the weight of the cheese taken from the moulds. The taste, odour and texture of the
cheese were assessed as close to that of traditional Camembert. The present method for making Camembert cheese using ultrafiltration is shown in Fig.1.

Whole milk - standardized pasteurized
↓
UF x 3 at 50 C
↓
Liquid pre-cheese
↓
+ starter 2% →
↓
Cool at pH 6.1
↓
UF from x 3 to x 5 at 30-35 C
↓
Liquid pre-cheese
↓
Penicillin
↓
Rennet
↓
Pour into mould
↓
Remove from mould
↓
Syneresis 20 h at 30 C
↓
Salting brine 30-45 min. → 20°C
Whey drainage (10% of the pre-cheese)
↓
Ripening (11 days)
↓
Cheese

Fig.1. Process for UF-Camembert cheese making

4.2. Cottage cheese

The various unsuccessful attempts have been made in the past to manufacture cottage cheese directly from a pre-cheese encountered difficulties in the cooking, cooling and creaming stages. The present approach is to make cottage cheese by reconstituting high concentrated skim milk with water or permeate. Pasteurize milk has been concentrated by a factor of 6.5 at 52°C to a total protein content of 20%. After storage the concentrate was reconstituted with warm tap water or permeate to protein concentrations in the region of 3-5% and then made into cottage cheese by standard methods. In quality the cheese was quite acceptable in flavour and appearance. The body was soft and smooth, though weak, but was better for the mixtures reconstituted to the higher protein levels. Reconstitution with water or permeate had no great effect
on cheese quality. Yields were 3.9-4.7 kg cheese per kg of total protein. From the water-reconstituted cheese, the whey had a lower BOD than whey in normal cottage cheese production.

4.3 Cream cheese

A technology has been developed for manufacture of cream cheese using ultrafiltration (Fig.2). Pasteurized skim milk was concentrated at 50°C to a solids content of 27.6% i.e. about 7-fold. Cream containing 67-69% fat was then added to bring the composition up to that of standard cream cheese. After inoculation with lactic acid starter cream cheese was made by the normal hot packed method, without any drainage of whey.

The method had certain advantages. There was an improvement in the yield of product, no fat loss, and a permeate which was easier to process than whey. The cheese had excellent shelf life. However, in some respects the cheese was not up to standard. Though smooth, it was considerably harder and more viscous than cheese made traditionally. It was of coarse texture, and scored low on taste due to carbonyl-like flavours.

Fig. 2 Process of cream cheese using ultrafiltration

<table>
<thead>
<tr>
<th>Skim milk, 100 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>↓</td>
</tr>
<tr>
<td>↓</td>
</tr>
<tr>
<td>UF X 3.3</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Lactic starte 1%</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Cream (40%) 38 Kg</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Permeate</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Pre cheese 41.7 kg pH 5.6</td>
</tr>
<tr>
<td>↓</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>NaCl, 0.23 kg</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Locust bean gum 0.23 kg</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

4.4 Feta cheese

Feta cheese is mindless, white, soft and salty, originally made from sheep milk in Greece. It is now becoming popular in Yugoslavia, Bulgaria and the Arab countries. Feta cheese from cow milk is being manufactured in most of European countries. Feta cheese manufacture is now the largest application of ultrafiltration in the dairy industry.
A flow diagram of the process is presented in Fig. 3. The milk was first pasteurized, partly homogenized and then preheated to 50° C in readiness for ultrafiltration. Concentration was to a factor of 5.1 providing a continuous flow of pre-cheese containing 39.5% dry matter. Drainage of small amounts of whey increased the solids content to 43%. There then followed a second pasteurization to kill the bacteria which had been concentrated during the ultrafiltration. The heating also slightly denatured the whey proteins which helped to develop the desired texture of the cheese. Homogenization assisted protein denaturation to the same end. Starter was then added at the rate of 2% of the volume of pre-cheese, and then the rennet, only 20% of the normal quantity being required. Curd formed within 20 minutes which was then cut and transferred to crates. No further whey was drained. Compared with the traditional way of making Feta cheese the improvement in the yield of cheese using the UF method was more than 30%.

Fig. 3. Flow diagram for UF Feta cheese making.

Whole milk standardized, pasteurised
↓
Pre-heat 50°C
↓
UF x 5.1
↓
Retentate
↓
Pasteurize 77°C
1 min
↓
Homogenize
↓
Cool 27°C
↓
Mould
↓
Syneresis 20 min.
↓
Salt
↓
Ripen
↓
Feta Cheese

2-3% Whey
The advantages of the process are therefore:

(i) Extra yield of cheese, 30-35%
(ii) Only 20% of normal quantity of rennet used
(iii) No fat loss in the whey
(iv) Automated continuous production possible.
(v) Quality of cheese good.

4.5 Mozzarella cheese

This is a fresh, semi-hard Italian type of cheese, formerly made from buffalo's milk but now mainly from cow's milk. The chief use is for pizza bakery and the largest production is in the USA. In considering the making of Mozzarella cheese using ultrafiltration it must be noted that there are two varieties, a high moisture type, 52-60% moisture, and a lower moisture type, 45-52% moisture. Naturally, the first attempts were for the high moisture variety. Initially the cheese failed to stretch in hot water, a fault attributed to the high buffering capacity of the concentrates and the large amounts of insoluble calcium in the cheese. The starting milk was therefore acidified to transfer more calcium into the soluble phase so that in the subsequent ultrafiltration more calcium was extracted with the permeate. A diafiltration step with brine was then added to assist in the same direction by exchanging calcium ions with sodium. Starter and rennet were then added to produce a coagulum to be worked up through the conventional steps for Mozzarella. The product had an appearance and texture similar to the standard and good stretching properties. An increase in yield of 16% over traditional production was obtained.

4.6 Quarg

Quarg is an unripened soft cheese and with a solid content of only about 20% manufacture by ultrafiltration would seem to be easily achieved. Two methods are possible, both aimed at improved yields by the incorporation of whey protein. In the first, traditional quarg is made as an initial step. Whey from this stage is concentrated by ultrafiltration to a solids content equal to that of quarg, namely 18%. The whey concentrate and the quarg from the first step are then mixed to form the final product. The yield is 26 kg cheese per 100 kg skim milk compared with 22 kg by the traditional method.

The second method is to make quarg directly from ultrafiltered skim milk concentrate. However, this has been hindered by bitter tastes developing in the cheese during storage, a defect due to excessive calcium. If quarg is made directly from the concentrates it contains 3 times as much calcium as normal. The difficulty has been overcome by first acidifying the milk to release some of the casein bound calcium which can then be extracted with the permeate during the filtration. The yield of cheese from the direct UF method goes upto 29 kg per 100 kg of milk.
4.7 Cheddar cheese

Cheddar is the most difficult variety of cheese to be made using ultrafiltration, yet it must be the goal for those countries where it is the preferred variety as in Britain, Canada, Australia, New Zealand and the U.S.A. As increasing degrees of concentration were used the quality of the cheese deteriorated in both flavour and structure. Upto a 2-fold concentration the cheese was satisfactory, at x3 it could be accepted but at x4 and x5 it could only be rejected. In flavour the cheese was described as "not Cheddar", it was dry, hard and curdy, and in structure it was coarse with fat not uniformly dispersed. The greatest advance towards making Cheddar cheese using ultrafiltration has been made by the Australian CSIRO Division of Food Research in Victoria. Milk is slightly acidified to pH 6.2-6.4 to reduce the mineral content, ultrafiltered to a 5-fold concentrate and finally diafiltered to reduce the lactose concentration to 3.3%. Only 22% of the normal quantity of rennet is required. The cheese making process contains all the traditional steps but the curd is much firmer and more brittle than normal curd. At this stage, special care and equipment is necessary to handle the curd, otherwise it is shattered causing high losses of fat and cascin fines. During the development of the process the curd could not be cut satisfactorily with a conventional knife. A stainless steel frame was fitted with cutting wires placed at 10 mm intervals which could cut the curd into 10 mm cubes. There is some whey drainage, about 10% of the normal quantity, with concentrations of fat and protein both at about 4%. The estimated total loss of protein from the starting milk is 16.5%, against 24% in traditional cheese making. This promises an increase in the yield of cheese. Organoleptically most cheeses have been acceptable in flavour at 16 weeks old. However, body defects have been detected at grading with such comments as weak, soft, mealy, pasty and sticky. Attempts are being made to improve the flavour and body and texture development in UF-Cheddar cheese by utilising modified starters and exogenous enzymes.

5. MANUFACTURE OF CHEESE BASE AND PROCESSED CHEESE

Cheese base is a paste of the same composition and pH as Cheddar cheese but without the Cheddar flavour and structure. It is used as the raw material in the production of processed cheese, replacing the young cheese component in conventional processed cheese manufacture.

The steps in the making of cheese base are as follows:

(i) Milk is pasteurized and standardized to 3.8% fat
(ii) Cool to 50°C
(iii) Ultrafilter to 30% TS.
(iv) Diafilter to reduce lactose to a level sufficient for subsequent bacteriological acidification to reach pH 5.2.
(v) Ultrafilter to 40% TS.
(vi) Re-pasteurize
(vii) Cool and 1% Cheddar starter
(viii) Evaporate on a swept surface evaporator to 60% TS.
The analysis of the cheese base will then be: TS 60%, fat 30%, protein 26%, ash 4%, water 40%, which is the same as the composition of Cheddar cheese. By this process the yield of cheese base is 18% more than that of Cheddar cheese from the same starting quantity of milk.

Processed cheese made by blending cheese base (80%) with 20% normal aged Cheddar has a satisfactory flavour but excessively firm body. Decreasing the proportion of cheese base to 30% makes a processed cheese satisfactory in all respects.

6. CHEESE POWDER

By means of ultrafiltration and drying, a milk powder can be produced for subsequent reconstitution and conversion into cheese. The main use is for export to those countries with low milk production and where the milk supply is very seasonal. The importing country then needs only to add water, starter and rennet to make cheese.

Cheese powder has three advantages:

(i) For under developed countries cheese production is simpler than expanding their dairy industries or setting up equipment for ultrafiltration.
(ii) The cheese making has no whey problem; this is left with the country performing the ultrafiltration which is more able to use sophisticated technology to make use of the permeate.
(iii) Transport of powder is cheaper than transport of cheese. The advantage is even greater if skim milk retentate powder is exported.

A comparison of the compositions of ultrafiltration retentate powder and skim milk powder, Table 32, illustrates the principles of this application of ultrafiltration. Retentate powder contains more protein and less lactose and its calcium content may be reduced by acidification of the milk before ultrafiltration. All these are essential steps towards making good cheese. The scheme for the production of cheese powder is given in Fig 4. The final cheese has been judged superior to that made from normal milk powder.

<table>
<thead>
<tr>
<th></th>
<th>Skim retentate powder (%)</th>
<th>Normal skim powder (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>62.8</td>
<td>35.7</td>
</tr>
<tr>
<td>Fat</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Lactose</td>
<td>23.9</td>
<td>49.3</td>
</tr>
<tr>
<td>Ash &amp; citric acid</td>
<td>8.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Water</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>kg powder/100 kg milk</td>
<td>5.2</td>
<td>9.5</td>
</tr>
</tbody>
</table>
7. CONCLUSION

UF cheese making is well established as a profitable method of making a limited equally to all cheese varieties. However, the advantages of UF cheese making do not apply equally to all cheese types and the balance between the advantages and disadvantages of making other varieties needs to be evaluated in each case. Extending the range of UF cheese on the market may not be a simple matter because incorporation of applicable quantities of whey protein, which is essential in order to gain a significant yield increase is counterparts. Differences are smallest in the case of low pH, high moisture cheeses, that are consumed while fresh or that do not rely solely on proteolysis for final product characteristics. Continuous efforts are being made to manufacture good quality hard and cheeses from UF milk employing certain process modifications and using modified starters.

8. REFERENCES

Green, M.L. 1990. The cheese making potential of milk concentrated upto four fold by ultrafiltration and heated in the range 90-97°C. J. Dairy Res. 57 : 549.


FUNCTIONAL PROPERTIES OF WHEY PROTEIN CONCENTRATES

Dr. Vijay Kumar Gupta
Dairy Technology Division, NDRI (ICAR), Karnal - 132001

1. INTRODUCTION

Proteins not only improve the nutritive value of the product, but also play functional role. Whey protein concentrates (WPC) exhibit excellent functional properties, provided care is exercised to minimise protein denaturation during their production. The important functional properties of WPC are: solubility, water binding, viscosity, Gelation, emulsifying, foaming, and buffering.

2. SOLUBILITY

Protein solubility is an important functional property of protein and is a valuable predictor for other functional properties. In general, protein solubility of WPC products prepared by membrane or gel filtration techniques is relatively high (88 to 100%). Considerable reduction of heat stability has been observed at higher protein concentration or with increased ionic strength. If salt is added progressively to an exhaustively (>90%) demineralised whey at pH values between 4.5 and 5.5, two macroscopic effects are observed. Initially, protein solubility increases (salting-in) and subsequently, after passing through a maximum, it starts to decrease (salting-out). The salting-in process is usually considered as a net increase of protein solubility on the basis of non-specific electrostatic interactions between a charged protein molecule and its environment.

Whey proteins are unique compared to many other proteins in that undenatured whey proteins remain in solution in acid, neutral and alkaline conditions. The solubility of whey protein products is impaired by thermal denaturation that occurs on heat treatment above 70°C at pH values between 4.0 and 6.5, and this has serious consequences for the foaming and emulsifying abilities of whey proteins. Heat treatments at pH values outside the above range are less detrimental to the solubility of whey proteins. Several terms are used to designate solubility of good proteins, of which the NSI (Nitrogen Solubility Index) and the PDI (Protein Dispersibility Index) are well known. Solubility of whey protein products is directly important in beverages.

3. WATER BINDING

The notions 'water-binding capacity' and 'water-holding capacity' of whey proteins are used interchangeably in the literature. Bound water is defined here as the water retained by protein-containing slurries following filtration on application of either mild pressure or centrifugal force. Real hydration water amounts to 0.3-0.5 g water/g protein and makes up only a small part of the total water bound in fresh or processed food products. A significant correlation exists between the total number of hydroxyl
and carboxyl, as well as basic groups and water binding. It is based on the immobilisation of water molecules via hydrogen bridges with polar groups. In addition to the water involved with charged groups and dipoles, water may be associated with hydrophobic groups contained in capillaries within the product or trapped within the food structure. The water-binding capacity of protein concentrates has been evaluated by a number of techniques. The most important of these are:

1. The filter press adsorption method, that involves placing a protein slurry on a filter paper between two Plexiglas plates. The plates are pressed and the area of the resulting ring of expressed water adsorbed by the filter paper is determined and is proportional to the amount of loose water in the slurry.

2. The centrifugation technique, that refers to the volume of water released when a homogenised protein sample, including some added water is centrifuged.

Water binding is important in baked goods, meat products and processed foods where water retention is desirable. In general, soluble whey proteins have a relatively low water binding capacity, which makes them useful in nutritional applications where significant quantities of WPC can be added without much changing the consistency of the product. Water adsorption increases with protein denaturation. Moreover, the water-binding and associated properties (i.e. swelling, viscosity and gelation) of proteins are the major determinants of texture in a number of (processed) food products. For water holding properties in food systems larger pore sizes, in the range of 100-2000 nm, are important.

4. VISCOSITY:

Whey proteins play an important role in controlling the texture of many food products. In this respect, the rheological and gelling behaviour of whey proteins are important determinants of their functional performance. The viscosity is important when whey proteins are used in viscous food products such as beverages, soups, sausages and custards. The viscosity of undenatured whey proteins in dilute aqueous solutions is governed by the shape and size of the molecules according to Einstein's equation:

$$\eta_s = \eta_o (1 + \beta \phi)$$

Where:
- $\eta_s$ = viscosity of the suspension
- $\eta_o$ = viscosity of the solvent.
- $\beta$ = shape factor (=2.5 for a spherical uncharged particle)
- $\phi$ = volume fraction of the protein in solution.

Whey proteins have minimum viscosity at pH 4.5 at room temperature. The relative viscosity of whey-to-water decreases between 30°C and 65°C. Above 65°C, this relative viscosity increases as a result of protein denaturation and above 85°C a further increase is observed as a consequence of protein aggregation. In a food process, protein solutions are frequently subjected to high degrees of shear and extremes of temperature. Shear exerted on dispersions of denatured whey proteins may break up
large aggregates and this can result in a decrease in viscosity. Therefore, the apparent viscosity in these systems provides, primarily, information about the extent of intermolecular interactions.

5. GELATION

Gelation is the formation of three-dimensional structure capable of entrapping sufficient water to produce the gel. Whey proteins, in their undenatured, soluble form, as in WPC prepared by milk processing treatments have the ability to form heat induced irreversible gels at appropriate protein concentration pH and ionic conditions. The gelation mechanism is two step that involves: (1) An initiation step involving unfolding or dissociation of the protein molecules, followed by (2) An aggregation step in which association or aggregation reactions occur, resulting in gel formation under appropriate conditions. For the formation of a highly ordered gel, it is essential that the aggregation step proceeds at a slower rate than the unfolding step.

The factors affecting gelation are various protein and non-protein components, pH, Ionic species, reducing agents, and heat treatments. The appearance of whey protein gels varies from translucent and elastic to brittle, aggregated, and curd like. Generally, translucent gels form at lower protein concentrations (3 to 5%) and at comparatively low heating temperatures (approximately 55 to 70°C). More aggregated, more opaque gels form at higher protein concentration (approximately 10%) and under more severe heating (above 90°C). Translucent gels also form at low ionic strength.

Gel formed by heating dialysed WPC are firmer, more cohesive, and more translucent in appearance than those formed by heating nondialysed WPC. Solution pH dramatically affects heat-induced WPC gelation. However, pH effects are interrelated with other compositional factors. Generally, gels formed with heating at low pH (pH, 6.0) are more coagulated and less elastic than gels formed at pH 7.0 to 9.0. Gel strength, however, decreases with increased solution pH from 7.0 to 10, and heat-induced gelation of WPC is inhibited at pH 11.0.

The general network structure, formed from irreversible heat-induced WPC gelation reactions, is related predominantly to disulfide bonding with some involvement of other non-specific bonding (hydrogen, hydrophobic and ionic) that are mediated by calcium.

6. EMULSIFICATION

Protein stabilised emulsions are essential in a wide variety of fabricated foods. WPC vary widely in their emulsifying capacity, both as a function of composition and processing. Neither undenatured or fully denatured whey proteins are highly effective emulsifiers. This can be attributed to the partial unfolding of the protein molecule through mild heating to expose hydrophobic regions that facilitate orientation of the protein at the oil-water interface. In general, sweet WPC are best for acid emulsions, such as salad dressing, whereas acid WPC are best for emulsions closer to neutrality (pH>6.0), such as coffee whitener. The criteria frequently used to describe emulsifying properties are emulsion activity (EA), emulsion capacity (EC) and emulsion stability (ES). EA refers to the maximum interfacial area per unit weight of protein of a
stabilised emulsion in carefully defined systems. EC denotes the maximum amount of oil that is emulsified under specified conditions by a standard amount of protein. ES refers to the ability of a protein to form an emulsion that remains unchanged during a certain period of time at a given temperature and gravitational field. The environmental factors that affect emulsifying properties of WPC are protein concentration, protein solubility, pH, salts, presence of other solutes and temperature. The ability of whey proteins to stabilise oil in water emulsions seems to be seriously affected by the pH and the ionic strength of the aqueous phase. At pH around isoelectric point, complete coalescence and phase separation occurs. Obviously, electrostatic interactions around the isoelectric point are responsible for protein aggregation and, as a consequence, the proteins are less flexible and, therefore, less prone to form a cohesive interfacial film.

Temperature is another factor that affects the emulsifying properties of whey proteins. In particular, the rate of diffusion to the newly formed interface and the rate of adsorption and unfolding increase with increasing temperature. Heating of WPC dispersions above 70°C either before or after emulsification, causes aggregation of whey proteins and is detrimental to their emulsifying properties. Heating of emulsions stabilised by whey proteins at concentrations higher than 6% causes gelation and occlusion of the fat.

6. FOAMING

Foaming may be defined as the creation and stabilisation of gas bubbles in a liquid. Essential for the formation of protein-based foams is a rapid diffusion of protein to the air-water interface to reduce surface tension, followed by partial unfolding of the protein. This results in the encapsulation of air bubbles and in the association of protein molecules leading to an intermolecular cohesive film with a certain degree of elasticity. These criteria are best fulfilled in whey protein products when the proteins are undenatured (molecularly soluble), not in competition with other surfactants at the air/water interface (e.g. fatty components), and stabilised by an increased viscosity when the foam has been formed (addition of water-binders). An optimum foam formation and foam stability in WPC is achieved at 25% dry matter, and with a protein content of 12 - 15%.

The various techniques that have been used to study protein foams may be classified as methods based on bubbling, whipping and shaking. The whipping method is preferred for testing most functional whey proteins, as it is the standard procedure for aeration of food products. The whipping properties of industrially prepared whey protein products are affected by several factors. The most relevant of these are: concentration and state of the whey proteins, pH, ionic environment, (pre-) heat treatment and the effect of lipids.

Aerated food products, such as whipped toppings, require rapid incorporation of air, a high level of aeration with a fine air micelle structure and a foam structure that is stable over time. The disturbance of whey protein foams by phospholipids and unsaturated fatty acids is well established. These lipids rupture the surface lamellae as a result of their higher surface activity and their thinning effect on the protein film. Most effective (polar) lipids may be tightly bound to proteins and this association is important to eliminate the detrimental effect of these free lipids. The presence of 1.5% or more of
lipid effectively suppresses whipping and foaming properties of WPC, and WPC with low lipid concentration will produce foams similar to those of egg white. Slight denaturation of whey proteins improves their whipping ability.

As the whey protein concentration is increased, the foam becomes more dense with more uniform air bubbles of finer texture. Generally, overrun increases with protein concentration to a maximum value after which it decreases again. For WPC foams, this maximum has been observed between 8 and 12% (m/v) whey protein. Denatured (aggregated) whey proteins lack the ability to diffuse rapidly to the interface and to re-orient for the formation of a viscous film. However, they may retard water drainage in existing foam lamellae (i.e. increase foam stability) and thus positively affect the balance between formation and breakdown of foams. The pH of the dispersion markedly affects the foaming properties of whey proteins. Maximum overrun and foam stability have been observed between pH 4 and 5. This feature may be explained by the maximum interpeptide electrostatic attractions of proteins around the isoelectric point. Provided the proteins do not coagulate, this interaction induces a cohesive protein film at the air/water interface, which increases the surface viscosity.

8. BUFFERING

The buffering effect, or buffering capacity, of WPC is significantly altered, not only by whey proteins, but also by whey salts and by possible residual quantities of protein precipitating polynons such as metaphosphates or carboxymethyl cellulose. Due to its phosphate and citrate contents, dried whey exhibits its greatest buffering capacity below pH 5.5. All whey protein preparations which have undergone significant demineralisation have a very low buffering capacity.

9. REFERENCES


HEAT STABILITY AND AGE GELATION OF MEMBRANE CONCENTRATED MILKS

Dr. A.A. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132 001

1. INTRODUCTION

As a biological fluid, milk may be considered extra-ordinarily stable. Its colloidal complex existing as micellar calcium phospho-caseinate has, in its native form and environment, a remarkable stability which enables production of sterilized milk and a variety of milk products such as ice cream, evaporated milk, condensed milk, milk powder as well as certain Indian dairy products including desserts. However, the stability of the casein micelles is sometimes inadequate in relation to certain products such as UHT-treated milk concentrates (Muir, 1984).

The colloidal stability of milk can be of consequence in two different ways so far as UHT-sterilized concentrates are concerned. First, the production process involving a high heat treatment (e.g. 135-150°C for a few seconds) may prove too harsh for the colloid to withstand without coagulation. Second, if the product could undergo such a heat treatment without getting destabilized, the colloidal complex may manifest its vulnerability through gelation (or sedimentation) during subsequent storage. Thus the success of UHT-sterilized milk concentrates depends on the ability of the process to minimize the chances of destabilization of caseinate complex during heating and ensuing storage.

2. HEAT STABILITY OF CONCENTRATED MILK

Heat stability refers to the relative resistance of milk to coagulation when it is heated at sterilization temperatures, usually 120-140°C (Singh and Creamer, 1992). It has been defined as the length of time that elapses between placing a small container of milk in an oil bath at a definite temperature and the onset of coagulation as indicated by flocculation, gelation, or changes in protein sedimentability or viscosity. Since pH is the most important single factor affecting heat stability, the measurement of the heat coagulation time (HCT) is generally made as a function of initial pH, and expressed as an HCT-pH profile.

The heat stability of unconcentrated milk may be expected to be indicative of that of the concentrated milk prepared from it. However, there appears to be no significant relationship between the two as noted by Singh et al. (1995).

2.1 Factors affecting heat stability relevant to membrane processing

Singh et al. (1995) listed the following factors influencing the heat stability of concentrated milks:
Compositional factors

- pH
- Total solids
- Protein composition
- Soluble salts

Seasonal variations

Processing factors

- Forewarming or preheating
- Homogenization

Additives

Many of these factors are interrelated and not all may be equally significant in relation to milk concentrated by a membrane process especially ultrafiltration (UF). The most relevant factors in this regard could be considered to be pH, soluble salts and lactose content as the compositional variables.

On concentration, the heat stability of milk decreases throughout the pH range of 6.2-7.2, and the decrease is larger with increasing concentration (Singh et al., 1995). The heat stability of buffalo milk concentrate is even lower than concentrated cow milk (Sindhu, 1995). One of the reasons for this decline could be the decreased pH of the concentrate. Soluble salts, calcium and phosphate in particular, are also believed to play an important role in the heat stability of concentrated milk as also of fluid milk (Fox and Morrissey, 1977). Newstead (1977) showed that a reduction in concentration of soluble salts in milk increased the heat stability of the resulting concentrate. This was confirmed by Muir and Sweetser (1978) who found an increased heat stability of concentrated milks from which soluble salts were partially removed by dialysis, before concentration of milk against water for short periods. Hardy et al., (1984) also reported that differences in the concentration of soluble calcium and phosphate had a pronounced effect on the heat stability of concentrated milks. Partial replacement of ionic calcium with sodium or potassium, considerably increased the heat stability of buffalo milk concentrate (Balachandran and Srinivasan, 1974).

McCrae and Muir (1995) noted that despite the lack of a significant direct correlation, lactose decomposition (resulting in pH drop among other effects) during heating is implicated in the heat coagulation process. Although no reports relate to concentrated milk, a few studies indicated that lactose tends to promote heat coagulation of unconcentrated milk (Pyne and McHearing, 1955; Sweetser and White, 1975). Kudo (1980) and Shalabi and Fox (1982) observed that in the absence of urea, lactose had little effect on the maximum heat stability. However, when urea was present, addition of lactose progressively increased the heat stability up to certain concentration (1-2%); at higher concentrators it decreased the heat stability. The normal lactose level in milk (approx. 5%) is well above that required for optimal heat stability.
2.2 Compositional characteristics of the membrane concentrated milks

Since composition-wise there is little difference between milk concentrated by evaporation and that concentrated by reverse osmosis (RO) the latter may not be expected to behave differently during processing or storage. Kocak (1985) reported slightly decreased ionic calcium content and correspondingly lower heat stability of RO concentrated milk. The milk concentrate obtained by ultrafiltration (UF), however, has a greatly altered compositional properties compared to conventionally or RO concentrated milk. Hence, the UF concentrated milk may conceivably exhibit potentially different heat stability characteristics.

Commercial UF membranes with nominal molecular weight cut-off values of 20 000-25 000 exclude all fat and almost all protein while permitting water, lactose, non-protein nitrogenous(NPN) compounds and soluble salts to pass through (Table 1). Thus protein and fat of milk are retained nearly completely in the retentate, whereas lactose, minerals and vitamins are partitioned between the retentate and permeate depending on the degree of concentration (Renner and Abd El-Salam, 1991).

Table 1. Average composition of milk and the UF permeate from it

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Milk</th>
<th>Permeate</th>
<th>Rejection coefficient(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>3.02</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>Protein</td>
<td>3.45</td>
<td>0.25</td>
<td>93</td>
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<tr>
<td>Lactose</td>
<td>4.51</td>
<td>4.50</td>
<td>0</td>
</tr>
<tr>
<td>Ash</td>
<td>0.60</td>
<td>0.49</td>
<td>29</td>
</tr>
<tr>
<td>NPN</td>
<td>0.07</td>
<td>0.025</td>
<td>62</td>
</tr>
<tr>
<td>Total solids</td>
<td>11.73</td>
<td>5.35</td>
<td>54</td>
</tr>
</tbody>
</table>

Yan et al. (1979)

Table 2. shows the compositional profiles of UF retentate and permeate from whole milk concentrated to different levels.

Table 2: Compositions of UF retentate (R) and permeate (P) from whole milk

<table>
<thead>
<tr>
<th>Volume conc. factor</th>
<th>Total solids (%)</th>
<th>Fat (%)</th>
<th>Protein (%)</th>
<th>NPN (%)</th>
<th>Lactose (%)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>12.9</td>
<td>3.9</td>
<td>3.1</td>
<td>0.18</td>
<td>4.7</td>
<td>0.77</td>
</tr>
<tr>
<td>P</td>
<td>5.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.18</td>
<td>4.8</td>
<td>0.53</td>
</tr>
<tr>
<td>R</td>
<td>28.6</td>
<td>12.6</td>
<td>9.8</td>
<td>0.18</td>
<td>4.1</td>
<td>1.3</td>
</tr>
<tr>
<td>P</td>
<td>6.1</td>
<td>0.0</td>
<td>0.09</td>
<td>0.19</td>
<td>5.1</td>
<td>0.53</td>
</tr>
<tr>
<td>R</td>
<td>43.3</td>
<td>21.8</td>
<td>16.1</td>
<td>0.18</td>
<td>3.2</td>
<td>1.9</td>
</tr>
<tr>
<td>P</td>
<td>6.7</td>
<td>0.0</td>
<td>0.49</td>
<td>0.19</td>
<td>5.2</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Glover (1985)
Retention coefficients for lactose are generally reported around 10% (Glover, 1985). Thus the lactose concentrated in the water phase of the feed rises as UF proceeds but the lactose level in feed dry matter decreases because proteins and fat are retained to much greater extents.

Minerals such as calcium, magnesium, phosphate and citrate are present partly bound to the colloidal complex and partly in solution. During UF, the bound portion is retained by the membrane and concentrated while the other portion passes through the membrane so that a constant concentration is maintained in the water phase of the retentate (Green et al., 1984). Because the concentrations of minerals in the water phase of the retentate remain unchanged, no transfer of minerals to or from the casein micelles occurs during UF. Concentration factors for minerals bound to the protein are therefore identical to those for the proteins. Thus the ratio of soluble calcium to total calcium in the retentate varies with the concentration factor and expressed as percentage, this ratio has been reported to be 29, 17, 11, 9 and 7 for concentration factors of 1, 2, 3, 4 and 5, respectively (Brule et al., 1984).

Retention coefficients for NPN are generally in the range of 20-40% but may be higher for high concentration factors (Glover, 1985). The NPN components permeated through the UF membrane are mainly urea and amino acids. Further the retention coefficients of skim milk for different constituents are similar to those for whole milks (Renner and Abd El-Salam, 1991).

2.3 Heat stability of UF concentrates

As mentioned above, the compositional alteration of milk concentrate obtained by UF as compared with the conventionally produced (evaporated) concentrate may be reflected in altered heat stability of the product. Swetsur and Muir (1980) observed that for skim milk the heat stabilities of milk concentrated to 9-15% TS by evaporation and ultrafiltration were similar. At 18% TS, however, the stability of UF concentrate was much better than that of the conventional concentrate, the HCT of the former being twice that of the latter. The difference in HCT increased as the concentration level increased. Since for similar TS level (say 18%), the protein content of the UF concentrate (12%) is appreciably higher than that of the evaporated concentrate (7%), at a comparable protein concentration the UF product would have much higher heat stability at all concentrations.

In-can sterilized concentrates prepared by UF of skim milk and containing edible carbohydrates could be produced with solids contents over 40% (Muir et al., 1984). However, when milk fat was incorporated into the protein-rich concentrates, the initial heat stability was often inadequate to obtain a homogenized, sterilized product. This stability could be enhanced by high temperature forewarming (150°C for 1 min), concentrate diafiltration, or by reduction of the total calcium phosphate content either (a) by solubilization of colloidal calcium phosphate through acidification (to pH 5.3) followed by neutralization with dilute solution hydroxide before concentration or (b) by citration of milk (20mM/l trisodium citrate added directly to the milk which was subsequently stored at 4°C for 24 h prior to
concentration (Table 3). Irrespective of the method used, a 33% reduction in calcium phosphate was achieved upon concentration (Sweetser and Muir, 1985).

Table 3 Heat coagulation time of UF concentrate obtained by different treatments (Fat:TS :: 0.3:1)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>HCT&lt;sub&gt;nat&lt;/sub&gt; (min at 120°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal concentrate</td>
</tr>
<tr>
<td>Control</td>
<td>23</td>
</tr>
<tr>
<td>Acidification + neutralization</td>
<td>44</td>
</tr>
<tr>
<td>Citration</td>
<td>64</td>
</tr>
</tbody>
</table>

Sweetser and Muir (1985).
*Heat coagulation time at natural pH.

Dialfiltration combined with solubilization of calcium phosphate was more effective than solubilization alone in increasing the heat stability. Calcium phosphate solubilization by citrate addition was more efficient than the acidification-neutralization method.

Glover (1985) suggested that UF concentrates would also remain stable to UHT treatment. In a recent study Patel (1993) observed that UF concentrates obtained from milk forewarmed at 120°C for 60 s were much more stable to UHT heating at 140°C for 5 s as compared to RO concentrates from the same milk. The RO concentrates with 30% or more TS were particularly heat labile and resulted in excessive fouling of the UHT plant making it impossible to run the process beyond a few minutes. On the other hand, UF concentrates having up to 33% TS could be subjected to UHT sterilization without difficulty also during the summer months when the RO concentrates were found to be even more unstable.

The improved heat stability of UF concentrated milk might be due to one or more of the compositional factors viz., decreased soluble salts and lactose concentrations and unaltered hydrogen ion concentration (and consequently higher pH of the UF retentate) attributable to the UF process. With regard to the concentrate pH, Muir (1984) noted that if the pH of skim milk concentrate (25% TS) was above 6.65, the product was stable to sterilization, but at lower pH values, it was rather unstable.

3. AGE GELATION OF STERILIZED CONCENTRATES

Loss of the colloidal stability in sterilized milk or milk concentrates during storage is manifested by gelation or sedimentation (Harwalkar, 1992). While sedimentation indicates precipitation of colloidal particles and settling, gelation is characterized by loss of fluidity (inverse of viscosity) through the formation of a coagulum or gel in the product during storage. Sterilized concentrated milk is generally more prone to age gelation than is sterilized milk. However, retort-sterilized concentrated milk i.e. evaporated milk is much more resistant to gelation as compared to the UHT sterilized product (Edmundson, 1970). Age gelation is the most important
single factor that has hindered the commercial production of UHT sterilized milk concentrate despite the fact that the technology was evolved as early as in the sixties.

3.1 Role of compositional variables in age gelation

Nearly all factors affecting the heat stability of concentrated milk have been found to influence age gelation as well. Variations in the compositions of raw milk have not been studied extensively in relation to their effect on age gelation of UHT-sterilized milk and concentrates (Harwalkar, 1992) presumably because of their relatively low significance. The composition of concentrated milk, however, may be considered more important from practical point of view.

The TS content, or more pertinently, the SNF content (Graf and Bauer, 1976) is perhaps the most important single factor influencing age gelation of concentrated milk (Levitz et al., 1963; Ellerton and Pearce, 1964). Increasing SNF greatly increases the tendency of the concentrate to age gelation. Not many reports are available regarding the effects of other compositional aspects. However, calcium has been reported to play an important part in age gelation. Addition of calcium chloride reduced the gelation-free life, whereas removal of calcium by dialysis improved the shelf-life (Morgan, 1963). However, milk concentrated to 25% by RO, having a slightly decreased ionic calcium level, gelled a little faster during storage at 25°C than did the concentrate (22% TS) obtained by evaporation under vacuum (Kocak, 1985). A role of the difference in TS in this case may not be ruled out.

3.2 Age gelation of UHT-sterilized UF concentrates

Patel and co-workers (1994) investigated the changes in viscosity of UHT-sterilized UF concentrated whole milk (24-34% TS) packaged aseptically in 250 ml glass bottles and stored at 18°, 30° and 37°C. The concentrates stored at 30° or 37°C did not show any increase in viscosity even after 40 weeks of storage. On the other hand, RO concentrates (28-30% TS) obtained from the same milk exhibited a sudden rise in viscosity after 8-10 weeks of storage and the product gelled within a few (nearly 8-10) days thereafter. This differential gelation behaviour of the two types of concentrates might be ascribed to the different ionic environment in terms of soluble salts and hydrogen ions.

During storage at 18°C, the RO concentrates did undergo age gelation, albeit at a slightly lower rate. The gelation-free life for these products was about 12-14 weeks. The UF concentrates stored at 18°C exhibited a gradual rise in viscosity after varying periods depending on the degree of concentration: concentrates containing 30-33% TS began to increase in viscosity after 16-18 weeks, whereas those containing less solids showed much greater resistance to gelation. This observed rise in viscosity of the UF concentrates (having 30% or more total solids) at 18°C might be attributed to the enzymatic gelation mechanism presumably operating in these products which could be conceived to have higher concentration of proteinases with temperature optima around 18°C. In contrast, the gelation of RO concentrates might have been brought about by the physicochemical or non-enzymatic mechanism operating in the presence of soluble salts and hydrogen ions in high concentrations (Harwalkar, 1992).
3.3 Age gelation of UF-RO concentrates

In order to retain more lactose while removing part of soluble salts by ultrafiltration, Patel et al. (1994) carried out partial concentration of milk by UF (25 or 50% volume reduction to achieve 17-18% or 22-23% TS, respectively) and further concentrated the UF retentates to 33-34% TS by means of RO. It was noticed that these concentrates, like UF concentrates, were appreciably stable against age gelation at 30° and 37°C, but tended to thicken after 8-10 weeks at 18°C.

4. CONCLUSION

The problems of colloidal stability of concentrated milk in terms of its ability to resist heat processing and age gelation need to be overcome if UHT sterilized concentrates are to be produced commercially. Among possible solutions, membrane processing appears to be a practical proposition. Concentrates obtained by ultrafiltration (UF) exhibit remarkably improved heat stability and resistance to age gelation when compared with conventionally concentrated milk, or concentrates prepared by reverse osmosis (RO). The combined process of concentration by UF-followed RO aimed at reducing the losses of milk solubles taking place during UF indicates the potential of the novel membrane process called nanofiltration in producing storage-stable UHT sterilized milk concentrates of high quality. Such a process, capable of bringing about partial mineral removal while retaining most of lactose and other soluble constituents of milk would presumably combine the advantages of both UF and RO from the viewpoint of enhancement of product stability during processing and subsequent storage into the permeate and minimizing the losses of lactose and other solubles.

REFERENCES


APPLICATION OF MEMBRANE PROCESSING: PROPHYLACTIC BIOLOGICALS FROM MILK

Dr. B.N. Mathur
Head, Dairy Technology Division, NDRI (ICAR), Karnal - 132001

1. INTRODUCTION

Recent research in Bio-chemistry, nutrition and physiology has brought into light, the extra-nutritional role that milk proteins play in maintaining the physiological normalcy of the body at organ and cellular level functions. Nature has endowed animals as well as humans to produce their own protective mechanisms against diseases. Bovine are unique in that not only can they produce anti-bodies for bovine diseases but also produce antigens to combat diseases suffered by other animal species. In other words, some of the minor constituents of milk also display a physiological function similar to drug principles. These differ basically from the modern chemical drugs which inevitably lead to untoward side effects, the most common of these being allergies of various kinds. The chemical drugs are, therefore, classified as the "unphysiological" drugs.

The physiological function of the drug principle from milk many a times may get destroyed to varying extent during routine processing depending upon the severity of heat treatment. A number of membrane oriented processes had been developed for the preparation and purification of drug principles from milk having pharmacological significance. The approach employed for processing of milk for the isolation purification of drug principles has to be done on pharmacological basis. Depending upon the degree of the denaturation during processing, the "health protective" quality of milk is further negatively influenced by environmental contaminants such as organo pesticides and insecticides.

2. PROPHYLACTIC BIOLOGICALS FROM MILK FOR THERAPEUTIC APPLICATIONS

A unique patented process has been developed at the University of Hamburg, Germany by Prof. K. Gauri, (personal communication) which allows the separation of milk into its Insoluble (Caseins and Fat) and Soluble (Whey protein, lactose, peptide and NPN) components. This separation is advantageous in the sense that the casein and fat fraction can be processed separately, avoiding the inevitable interaction between the casein and whey protein fractions under the influence of heat. This approach allows reconstitution of milk with "bio-protective factors" intact. Alternatively casein and fat rich retentate can be used for cheese production and the whey protein permeate can be ultrafiltered to obtain undenatured whey protein isolates of extremely high purity (pharmaceutical grade) displaying prophylactic quality. Various prophylactic biological preparations mentioned above have been tested under medical supervision to treat or prevent a range of human ailments such as arthritis, toothache, allergies, various kinds of viral infections such as common cold etc.
The initial conceptual approach was developed in New Zealand through collaborative programmes between Stolle Milk Biologics and New Zealand Dairy Board. Cows were injected with a particular antigens and left to develop immune system for the disease these cause. The milk from the herds of bovine so treated was processed to isolate and purify the anti-bodies. These anti-bodies are eventually used for preparation of suitable forms of application for administrating to the human subjects. The anti-bodies also help the human body to build up its own defences against diseases. Such preparations have been successfully utilized to combat various types of gastric disorders, diarrhoea and vomiting as well as to reduce high blood pressure and inflammation which creates pain in arthritis sufferers. Conceptual approaches have been developed for the preparation of pharmacological principles from milk proteins which will help to lower blood cholesterol levels and be effective in preventing acne. Extensive tests so far have shown no side effects when used in treatment of any of the nominated diseases. The official slogan "Milk is good for use" has never been so apt.

3. MILK PEPTIDES WITH CARDIOVASCULAR ACTIVITY

Functional similarities between milk and blood coagulation as well as sequence homologies existing in γ-fibrinogen chain and κ-casein were the basis for the approach which various researchers have adopted to demonstrate the cardiovascular activity of a peptide family issued from this milk protein. These peptides are located in the glycomacropeptide segment of κ-casein. They are able not only to inhibit platelet aggregation but also to combine with receptor sites and consequently to prevent fibrinogen binding with blood platelets (anti-thrombotic activity). In vitro antiaggregatice activity is reinforced by the by the presence of a Lys residue in the sequence; therefore, the 112-116 peptide resulting from tryptic hydrolysis of GMP seems to be 200-fold more active than the 113-116 sequence. Hydrolysis of angiotension-I by angiotension covering enzymes (ACE) is the key step in the physiological regulation of blood pressure. Peptidic sequences able to block ACE action with a view of finding therapeutic natural substances acting against blood hypertension have been investigated. Such peptides are located in β-casein, and some, such as the 43-52 human β-casein sequence, seem to be very efficient. The biological activity of milk proteins seems to be an increasingly plausible possibility, given the results acquired during the last decade, which besides the demonstration of specific activities in vitro and in vivo, indicate the multifunctionality of certain sequences and the conservation of specific sequences in milk proteins produced by many mammalian species.

4. BIO-ACTIVE COMPONENTS FROM CHEESE WHEY

Economic utilization of whey solids has seen serious techno-economic challenges to the dairy industry engaged in the manufacture of cheese, cascin pancer and chhana. During the Post-GATT period prices of commonly prepared products from whey i.e. whey protein concentrates and lactose have become very competitive, which has adversely affected the prices of whey products on a global basis. Newer R&D efforts are being made for the utilization of whey with refined whey protein components intended for unique functional and pharmaceutical applications, which may permit greater value addition. Lactoferrin and lactorperoxidase have a very high market value as fine chemicals as functional foods as well as pharmacological products.
Recent developments in membrane processing have paved way for the industrial preparation of 'nutra-ceuticals' such as LF and LP and high purity, more than 95% and of pharmacological quality.

In the middle of the 1980s the former Research Department of the Swedish Dairies' Association started R&D activities to look at the options of isolating LP and LF. This work led to the creation of a now world wide patented industrial process. This process has been commercially applied on an industrial scale for more than 4 years at the Kristianstad dairy plant belonging to Skanemejerier, giving products of high purity, > 95%, and good quality. Below some of the basic steps described in the patent document in our process of isolation of LP and LF and milk phospholipid separation will be discussed. The basic principle underlying the process is the fact that both lactoferric and lactoperoxidase have isoelectric points (pI) of the whey proteins have pI in the range 4.2-5.3. A fundamentally suitable process for isolation of lactoperoxidase and lactoferrin is therefore to expose the whey (pH 6.2-6.6) to a cation exchanger for selective adsorption. Use is made here of the net positive charge of LP and LF in contrast to the other whey proteins, which have a negative charge in this pH range. By charge interaction the LP and LF molecules bind to the negatively loaded functional groups of the cation exchanger, leading to a fixation of these molecules on the ion exchange resin while the other whey proteins pass through, because these are negatively charged.

In order to create an industrially viable process some basic criteria have to be fulfilled. One of them is the need of a particle-free whey in order to keep a high flow rate during the loading phase because very large volumes of whey have to pass the ion exchange column. The contents of LP in ordinary sweet whey is about 20 mg/l and LF about 35 mg/l, which means that with a theoretical 100% yield 50 m of whey has to be treated to get 1 kg of LP and about 30 m for 1 kg of LF. The capacity of used ion exchange resin is equivalent to adsorption of 40-45 g of LP plus LF from whey per liter of resin can pass the ion exchange column during 15-20 hours per ion exchange cycle.

Pharmaceutical Applications Of Lactoferrin: The bio-protective nature of LF is of great significance in products such as infant formulas, health foods, skin creams, and as an antimicrobial product. Another significant development in field of cancer is the potential beneficial application of LF for treatment of Leukemia. It has been postulated that in association with the human γ-interferon, LF suppresses early human monocyte or mono-blastoid cell line (Bronnemeyer, 1985). LF also enhances the action of certain antibiotics which enhances the efficacy of pharmaceutical preparations.

5. BIOLOGICALLY FUNCTIONAL PEPTIDES DERIVED FROM MILK PROTEINS

Typical opioid peptides and other functional peptides derived from milk proteins have bi- or tri-functional roles. Opioid agonist peptides bind to opioid receptors and exhibit morphin-like activity. They can be detected by their inhibitory action on electrically stimulated contractions of the guinea pig ileum longitudinal muscle-myenteric plexus. The first characterized opioid agonist peptides from milk protein were Tyr-Pro-Phe-Pro-Gly-Pro-Ile and Tyr-Pro-Phe-Pro-Gly. These peptides
correspond to the 60-66th and 60-64th residues of bovine $\beta$-casein, and are termed $\beta$-casomorphin 7 and 5, respectively. The letter is about five times more active than the former. Similar opioid peptides were found among the fragments of human $\beta$-casein.

An opioid peptide from bovine $\alpha_{\text{c}}$-casein, derived from the 90-96th residues was termed $\alpha_{\text{c}}$-casein exorphin. Many opioid antagonists among fragments of bovine and human k-casein and human lactoferrin have been produced by chemical synthesis and enzymatic digestion. These peptides bind to opioid receptors but do not exhibit opioid agonist activity. The function of these peptides is to antagonise the action of opioid agonists. Another tetrapeptide amide, morphiceptin is most active opioid agonist in the bovine $\beta$-casomorphin group. This group also includes three antagonist peptides having residues with esterified - carboxyl groups. Esterification occurred during the extraction process. The antagonist activities of these peptides are small when the carboxyl groups are free.

The effect of plasmin and chymosin on $\alpha_{\text{c}}$, $\beta$, and whole casein have been investigated in simulated milk serum at pH 6.6 (for plasmin) and pH 5.3 (for chymosin). At these optimal conditions both plasmin and chymosin hydrolysed the available caseins very intensively. Electrophoretic analysis showed that plasmin hydrolysed $\beta$-casein completely after 6 h and $\alpha_{\text{c}}$ casein only after 240 h. A complete degradation of the intact caseins by chymosin at pH 5.3 was reached already after 21 h. Peptides of molecular mass of 5000 were formed slowly by plasmin only after 72 h (hydrolysis of $\beta$-casein) and after 144 h (hydrolysis of $\alpha_{\text{c}}$ -casein). Towards $\alpha_{\text{c}}$-casein chymosin showed a particular specificity producing 7 peptides (rel. molecular mass is 5000) after 21 h of incubation. Additional studies showed that the electrophoretically detectable plasmin degradation products of $\alpha_{\text{c}}$ -casein were rapidly hydrolysed by chymosin after the change of pH-value. The proteolytic specificity of plasmin (fibrinolysin, E.C. 3.4.31.7, from bovine plasma) on bovine $\alpha_{\text{c}}$ -casein was determined. The principle plasmin cleavage sites were found at Arg-22-Phe-23, Arg-90-Tyr-91, Lys-102-Lys-103, Lys-103- Tyr-104, Lys-105-Val-106, Lys-124-Glu-125 and Arg-151-Gln-152. The initial cleavage sites and order of production of small (pH 4.6-soluble) peptides suggest that $\alpha_{\text{c}}$-casein was cleaved initially towards the centre of the molecule.

It has been found recently that two peptides derived from serum albumin and $\beta$-lactoglobulin induced contraction of guinea pig ileum longitudinal muscle when the test was done without electric stimulation in the absence of agonist. They call such peptides, "peptides acting on smooth muscle". Two opioid antagonists, casoxin C and D, also belong to this group. Peptides have been found that inhibit angiotensin I-converting enzymatic hydrolysate of casein. ACE converts angiotensin II to II; the latter is a very hypertensive peptide. This enzyme also hydrolysis bradykinin, which is a hypotensive peptide. Thus angiotensin I converting enzyme inhibitors [ACEI] are antihypertensiura peptides. A 69 peptide fragments of human $\beta$-casein and 23 of human k-casein has been synthesized. Peptides within the sequence [39-52] of human $\beta$-casein and [63-65] of human $\kappa$-casein have potent inhibitory activity. The most potent inhibitor is a decapeptide, Ser-Phe-Gln-Pro-Gln-Pro-Leu-Ile-Tyr-Pro [residues 43-52 of human $\beta$-casein], which is also active in vivo.
Phagocytosis-stimulating peptides have been found among fragments of β-casein. These peptides stimulate in vitro phagocytic activity of murine and human macrophages and exert in vivo a protective effect against Klebsiella pneumoniae infection of mice. Peptides which inhibit both aggregation of ADP-treated platelets and binding of fibrinogen to ADP-treated platelets have also been identified. Peptides which stimulate DNA-synthesis of BALB/c 3T3 cells in tryptic hydrolyzates of human and bovine β-casein, their mechanism is not clear. The procedure for large-scale preparation of glycomacropeptide [GMP] from rennet casein whey has been reported recently, since GMP may be utilised as an ingredients of dietary food an pharmaceuticals. Extensive studies on casein phosphopeptides showed that CPP prevents the precipitation of calcium phosphate and increases the concentration of soluble calcium in the small intestinal lumen of rat. CCP, injected into the lumen of a ligated loop of small intestine, enhanced absorption of calcium from the loop. On the other hand, in vivo experiments using synthetic phosphoseryl peptide on absorption of calcium by rat showed that CPP does not stimulate intestinal calcium absorption in rats eating a normal meal. The 47Ca/47Sc ratio method was used in this study. It has been suggest that the physiological role of CPP in intestinal calcium absorption may be only an indirect luminal inhibition of the precipitation of calcium phosphate. A moderate and exchangeable binding of Ca to the CPP molecule well substantiates the high absorbability of calcium from milk and dairy products. Future studies of milk proteins and their peptides should provide valuable new insight into their influence on various metabolic processes, and new aspects for consideration in evaluating the nutritive value of milk proteins. The physiological importance of the bioactive peptides derived from milk proteins is not yet wholly understood. However, it is possible that these peptides play a significant role in regulating such posses as intestinal motility, hormone release, or nutrient absorption in the newborn. Studies on protective proteins in milk and protective peptides derived from milk proteins should be encouraged. Application of these studies will contribute a great deal to human welfare.

6. PHOSPHO-LIPIDS FROM MILK

Swedish Dairy Industry has also developed patented technology for the recovery of milk phospho lipids in highly refined form for whey fat. A product with enriched phospho lipid content displays excellent emulsifications properties. This property can be utilized effectively in various functional foods and pharmaceuticals. Another interesting component in the whey fat fraction is Sphingomyelin which displays potential bioactive properties. Membrane processes permit preparation of sphingomyelin with more than 95% purity.

7. CONCLUSIONS

Bio-active substances in foods represent "extranutritional" constituents naturally present in small quantities in the food matrix, produced upon either in vivo or industrial enzymatic digestion, the latter being a result of food-processing activities. Bio-active constituents of food evoke physiological, behavioural, and Immunological effects. Evidence from both epidemiological and animal studies has suggested chemo-preventative roles for phytochemicals in certain forms of cancers and in the control of hyperlipidaemia. Secondary products of plant metabolism can modulate xenobiotic metabolising and cholesterol synthetic enzymes. Unique physicochemical
properties of food-derived peptides with characteristic amino acid composition and sequences have been reported to influence intestinal transit, modify nutrient absorption and excretion, and exhibit immuno-stimulating and antihypertensive activity. Biologically active peptides derived from casein, fish muscle, and plant protein hydrolyzates have been isolated, purified, and identified in peptide sequence studies. Therapeutic proteins (e.g., specific antibodies) derived from animal products such as milk may offer the potential for developing specialised food products with prophylactic as well as nutritive quality. Membrane processing permits the isolation and preparation of various bio-active substances that permit tremendous value addition for application in the pharmaceutical, cosmetic and functional foods industry.

8. Selected References

UTILISATION OF WHEY PROTEIN CONCENTRATES IN DAIRY AND FOOD PRODUCTS

Dr. Vijay Kumar Gupta
Dairy Technology Division, NDRI (ICAR), Karnal 132 001

1. INTRODUCTION.

There has been a continuous increase in WPC production since the introduction of the latest ultrafiltration process about three decades ago. It is now a major means of WPC production throughout most of the dairy countries of the world. At present, nearly 12% of the total whey utilised is processed by ultrafiltration. Ever increase in WPC production may be attributed mainly to the greater efforts on the part of whey producers to abide by pollution regulations and to the emergence of reliable, hygienic ultrafiltration plants and the refinement of continuous operations using multi-stage recycle loops and diafiltration.

Increased production of WPC warrants its greater application in food products. Though soluble WPC have been found to be technically suited to a wide range of products, its use is not cost effective in all cases. Presently, WPC constitutes a very small proportion (10%) of protein utilisation in food industry. More product formulation work, specially in the food industry, is needed to move WPC into the general market place. The largest potential use of WPC is as a replacement for non-fat dry milk (NFDM) in the food industry. WPC with 35% protein is perceived to be a universal substitute for NFDM, because of the similarity in gross composition and its dairy character. Superiority of WPC over NFDM is also due to cost advantage. WPC can also be seen competing with casein, egg albumin and soya proteins within the existing markets. The PER value of whey proteins (3.2) is very high compared to standard casein (2.5).

2. HUMANISED MILKS

Due to various reasons, buffalo and cow milks are being humanised and used partly or exclusively for feeding human infants throughout the world. For humanisation, apart from making other modifications, whey proteins proportion needs to be increased in these milks. For this, a great potential lies in the application of WPC. In two of the three patents for humanisation of cow milk, Morinaga Milk Industry Co. Ltd. of Japan indicated the addition of whey proteins and lysozyme. Ivanov et al. (1971) also described the supplementation of high quality whey proteins for formulation of two humanised milk formulae "Bebe O" and "Babe 1" from cow milk.

A UK patent covers whey protein preparations which are heat stable at neutral pH and suitable for increasing the protein contents of infant formulae and beverages. Whey which might have been demineralised or ultrafiltered, is processed to adjust its salt balance before or after concentration by evaporation. Adjustments in
minerals concentration are achieved by additions of citrate, phosphate, a food acid or by diluting the whey proteins with water.

3. CHEESES

The cheese manufacturing industry has considerable interest in developing applications to use WPC. Ultrafiltered and denatured liquid WPC have been added to milk for cheese making. The yield of cheese is improved but the quality of cheese made have been generally unsatisfactory. Addition of WPC (10-12% protein, 6-6.5% lactose and heated to 85-87°C) to milk resulted in poor structure of Danbo cheese (Birkkjaer et al., 1974). Abrahamsen (1979) manufactured Saint Paulin cheese with added liquid WPC containing 14% total solids and 8.75% protein. All experimental cheeses exhibited a loose and doughy body and some cheese had a sour off flavour. Yields were 1-17% greater. Brown and Ernststrom (1982) reported an increase in the average yield of cheddar cheese by 4% with the addition of WPC (9.8 and 20.3% total solids and denatured) to milk. Experimental and control cheese did not differ significantly in any flavour or body-texture defects except acid. Banks and Muir (1985) manufactured Cheddar cheese with added acidified WPC and observed a maximum increase in yield of 7%.

Baldwin et al. (1986) reported the reconstitution of two WPC powders containing 35 and 55% protein to a 15% (w/v) suspension, heat treatment at 70°C for 15 min. and addition of 5-10% denatured WPC suspension to milk for Cheddar cheese manufacture. Cheese yield increase was 1.4-6.2% above those of the control on a 63% total solids basis. With increased WPC, there were more flavour defects in cheese. The most common criticism was atypical (unclean) cheese flavour.

A patent from Netherland described the production of fresh cheese or products containing fresh cheese with a high protein content by adding a WPC obtained through ultrafiltration. Kuipers and Schroder (1980) reported the dispersion of WPC (pH 2.5-3.7, heated to 80-95°C) in unripened cheese curd.

Georgakis (1975) reported the preparation of good quality processed cheese from Feta cheese with the addition of 5-20% WPC. At Federal Dairy Research Centre in Federal Republic of Germany, Gupta and Reuter (1986) standardised the manufacturing process of good acceptable quality of processed cheese foods from Cheddar cheese by 20% of cheese solids replacement with those of WPC. These workers observed an increase in hardness in processed cheese foods with the increase of WPC solids. The melting quality of the product deteriorated with the increased WPC addition. Thapa and Gupta (1996) also made similar observations in India.

Canadian Scientists at the University of Guelph reported the development of WPC, which has been utilised successfully in cheese spreads and other cheese foods.

4. FERMENTED PRODUCTS

Jelen et al. (1987) reported decreased viscosity of yoghurt with increasing amount of WPC. Greig and Harris (1983) also observed that the replacement of 40% of liquid milk with WPC gave Yoghurt of lower viscosity. Odour, taste, appearance
and consistency were not affected by substitution of 10% WPC. Later, workers at Massey University, New Zealand concluded that the addition of up to 15% WPC (20%, if the preheating step is modified) would enhance the desirable property of natural set yoghurt. In general, the addition of WPC resulted in a firmer yoghurt with less syneresis, but yoghurt made with more than 20% WPC exhibited slight graininess. Abd-Rabo et al. (1987) reported increase in sensory score of yoghurts manufactured with 15-40% WPC (3.9% protein) addition.

Chojnowski et al. (1978) reported the production of yoghurt, kefir and frokren by adding WPC. Products had better structure and organoleptic property than traditionally made products.

5. ICE CREAM AND FROZEN DESSERTS

WPC have been used to replace milk solids-not-fat in a variety of ice cream formulations. With the addition of WPC, there is an increase of albumin and globulins in the mix which improve the quality of ice cream and frozen desserts by eliminating shrinkage problems. Lando and Dahle (1949) attributed the shrinkage of ice cream to lower level of albumins and globulins in ice cream mix. Hugumin (1987) reported that ice cream in USA can include up to 25% of milk solids-not-fat as WPC.

Ice cream prepared with 50% skim milk powder and 50% WPC and lactose hydrolysed skim milk powder scored best in creaminess, smoothness and full of flavour (Huse et al., 1984). Addesso and Kleyn (1986) observed low sodium content (30.5 mg/100 g compared to 81.5 mg/100 g) in high quality vanilla ice cream, prepared with the partial replacement of dried skim milk with WPC. In an European patent, production of desserts having good flavour and texture characteristics have been claimed by partially replacing dried skim milk and stabilisers with modified WPC (denatured). Zall (1992) pointed out that encapsulating WPC proteins gives a fat-like mouth-feel which makes this form of WPC useful for making non-fat or very low-fat frozen desserts.

WPC can be used in milk chocolate flavoured coatings. Compound coatings are used on frozen desserts to give proper coating, hardening and texture (Edwards, 1984). Hugumin (1987) advocated the incorporation of WPC in juice bar mixes. The author pointed out that protein provides lubrication to water ice mixes and reduces wear on continuous freezers. Further, WPC facilitates low over run into juice bar mix and thus reduces the hardness of the bar. In addition, level of protein can be adjusted from giving no discernible flavour change to that which produces a different dairy like flavour.

6. MEAT PRODUCTS

For meat industry, WPC should have good protein solubility and as low coagulation temperature as possible with minimum protein content of 35%. Downes et al., (1981) observed promising results with the use of denatured WPC as a meat extender in processed meat products.
USSR Scientists in 1980 showed that WPC may be used as a protein additive in cooked sausages with a short shelf life. Addition of WPC in emulsion-type sausage product increased fat binding properties, product firmness and improved flavour, texture and juiciness. (Ensor et al., 1987). Hugunin (1987) reported that WPC may be added to the batter of comminuted meats to aid in emulsification, fat binding and water binding. Excellent bolonga and frankfurters have been prepared with WPC. DeWitt (1984) observed that meats may be injected with a WPC solution and massaged or tumbled to reduce weight loss in the product.

7. BAKERY PRODUCTS

Whey proteins have been considered as a potential ingredient for the bakery industry in view of their desirable functional characteristics and nutritive value. After adequate heat has been applied, the whey proteins can be used in bread, biscuits and cakes, but the addition of whey proteins to dough does lead to volume depression and to a more glutinous texture. Isolated whey proteins increase the hardness of wheat-based doughs and produce a lighter coloration. They can be used, because of their good functional properties, as a partial substitute for egg protein powder; the replacement level constituting 30-40%. Sanchez et al. (1982) emphasised the nutritive advantage of supplementation of bread with WPC. They observed a reduction of relative bread volume when WPC (35-60% protein) was added at 2, 4, 6% in wheat flour before baking. Another report described that WPC addition in bread resulted in loaf volume reduction, increased protein and amino acid contents and that the bread was acceptable.

Renz-Schauen and Remmer (1987) discussed the fortification of bread using different types of WPC. Three WPC's were heated at 3 different temperatures (63, 70, or 78°C) for 30 min., spray dried at inlet and outlet air temperatures of 150 and 85°C respectively and added to wheat flour. Bread protein content increased from 12.8 to 15.9% and the chemical score of the bread protein increased from 36 to 66, depending on the amount and protein content of the added WPC.

Bread made with controlled heat treated WPC, for partial denaturation of whey proteins, have been reported to be of better quality. Optimum heat treatment observed was 85°C for 15 sec. or 75°C for 60 sec. Sanchez et al. (1984) observed an increase in the elasticity of doughs with the use of higher heat treated WPC at increasing concentration. However, water absorption of doughs decreased by increasing concentration of WPC.

Lauck (1978) opined that protein enriched and with lower shortening content, leavened baked goods can be prepared with unedenatured WPC. Towler (1982) experimented with the incorporation of unedenatured WPC in the formulation of noodles. WPC at 10% level gave a very sticky dough making it difficult to process, but produced significantly harder to dry noodles with enhanced colour. These noodles might hold up to freeze thaw cycling and microwave oven. Compression testing of dough indicated that moisture content had a large bearing on strength and elasticity. The adhesiveness of dough was significantly higher with the incorporation of WPC. A US patent covers the preparation of high protein biscuits with a protein content at least 20% higher than that of normal biscuits by incorporating oxidised WPC.
A number of researchers have investigated the possibility of replacing egg white with whey proteins in the manufacture of cakes with varying degree of success. Richert (1973) carried out studies for the complete replacement of egg albumin by whey protein isolates for making white layer cakes. The resultant product exhibited similar cake volumes and profiles as the cakes made by using egg albumin. However, cakes prepared with whey protein isolates appeared to be more tender, moist and crumbly. Angel food cake, however, could not be prepared of good quality by replacing egg white with WPC. Although the batter containing WPC had greater volume compared to the one containing egg, it collapsed during baking. This was attributed to the interaction with the ingredients of angel food cake during baking as a result of which WPC lost their form stabilising ability. There has been an evidence of the presence of loaf volume depressant factor in the whey proteins.

WPC can also substitute egg white for the manufacture of meringues and macaroons. Using WPC to raise the protein level of macaroni from 13% to approximately 20% resulted in an adjusted PER exceeding 2.5. However, γ-globulins, which are present in WPC, have an adverse effect on the quality of these products. Therefore, γ-globulins should be denatured for incorporating in such bakery products.

8. READY TO EAT CEREALS, CONFECTIONERY PRODUCTS, SNACK FOODS AND SAUCES

Addition of 4% whey proteins to corn, wheat or rice would about double the protein efficiency ratio of these cereals. Further, whey proteins compared with many other proteins are less likely to mask added flavours. Renz-Schauen and Renner (1987) reported that the fortification of cereals with WPC (average calcium content, 500-700 mg/100 g) substantially increased the calcium content.

Edwards (1984) discussed the problems and possibilities of using various whey derived products in confectioners manufacture. In U.S.S.R., partially demineralized acid WPC with 50% protein (on dry matter basis) is used to replace egg white in whipped products and other WPC is used in confectionery products. Wingered (1971) reported the production of high protein (WPC) snacks. Hugum (1987) observed that cheese fillings and dips require a creamy texture, low water activity for shelf stability and good cheese flavour. For better flowability, cheese, when mixed with oils, looses some of its flavour. Softer cheese, with lesser flavour loss, can be produced by mixing WPC, which don’t coagulate on mixing with cheese. Whey proteins tend to complement cheese flavours. Jasinki and Kilara (1985) reported that whey proteins should bind cheese flavour. Whey proteins are reported to be less prone to cook on walls, minimise requirement for agitation and stabilise sauces and gravies subjected to freeze-thaw cycles. Whey proteins also provide dairy flavour to cheese and cream sauces and to gravy type sauces.

9. ACID FOODS AND BEVERAGES

Solubility of WPC at low pH, a unique property among proteins, allows it to function in acid foods and beverages, where NFDM and casein cannot. This opens the door to the use of WPC as a source of protein in such products as fruit jams, Jellies, fruit juices, carbonated beverages and other soft drinks. Zheltovskaia and Ivanova
(1983) pointed out that WPC have high biological value and that it is reasonable to use them for the enrichment of acid products and drink mixtures, which require preliminary hydration prior to their utilisation and consumption. These products are with high per capita consumption and normally contribute little or no protein to the diet. If WPC penetrates even a fraction of these products, there won't be any WPC left unutilised. Holsinger et al. (1973) reported that soft drinks can be fortified with 1% whey proteins without detectable change in flavour. Products containing electrodialysed WPC exhibit greater viscosity during storage than those with ultrafiltered WPC.

Kravchenko (1988) pointed out that utilisation of ultrafiltered WPC in drink manufacture ensures the more rational usage of undeveloped whey proteins in food. Beverages based on ultrafiltered WPC have high nutritive and biological value as well. Costamagna and Rossi (1980) mixed reconstituted WPC (10-20%) with milk in the ratio of 1:1 or 1:4. The beverage prepared had increased protein, reduced residual lactose and good organoleptic quality. Rossi and Costamagna (1981) developed a range of fermented milk beverages on the base of WPC. In the USSR, a wide range of drinks using WPC, fruit juices, citrus and special herbal infusions reputed to have biological-active substances, have been developed. The drinks have pleasant taste and aroma, are very nutritious and have increased protein content as well.

A mixture of cows' skim milk and dry WPC is the base of a drink, which resembles mares' milk "Kumys" in its flavour. The mixture is inoculated with 7 strains of micro-organisms. The beverage is like dry sparkling wine. Its refreshing qualities are increased by the addition of fruit juices, particularly by the orange and grape fruit juices. In Federal Republic of Germany, medicinal whey beverage sells under the brand name of "Plus". This beverage with whey proteins additive contains young starter culture (Sanoghhurt), which is reputed to have therapeutic value.

Express Foods (USA) manufactures WPC as a base for the drinks with 75 and 50% protein content. When dispersed in cold water, the WPC contribute to pH stability and are soluble in acid medium with no off flavours. The above WPC have light aroma and contribute to a minimum viscosity of the solution at the room temperature with a colour. It is felt that drinks for school breakfast, yoghurt and liquid milk products analogues are ideal for protein enrichment.

Foremost Foods Co. (USA) has developed the technology for powdered WPC with 35% protein content. The above product is dispersed in acid and alkali medium readily, contains some ash and has pleasant taste. The above dry powder is used for the manufacture of refreshment type drinks of the increased protein content. Dry WPC is utilised in dry sparkling drinks manufacture, as well as, in different fruit mixtures. The reconstituted drinks contain about 1% whey protein.

Hugunin (1987) reported that WPC was included as a protein supplement in a powdered orange beverage "Samson" and marketed in developing countries by Coca Cola. WPC was also included as a protein supplement in a frozen orange juice concentrate "Pro Power" and market tested by Nabisco.
10. OTHER PRODUCTS

McDonough et al. (1976) used WPC as milk extender. Upto 40% of WPC from sweet whey or 20% from acid whey could be blended with skimmed milk without adversely affecting the organoleptic quality. In a U.S. patent, modified WPC (50% protein) is used as a binding agent in a processed food containing a blend of edible textured protein particles, including single cell protein.

WPC are receiving considerable attention as the base material for the preparation of a variety of dietetic and therapeutic products. Delaney (1976) cited that electrodialysed WPC finds use in the treatment of chronic uremia. He also quoted the use of a whey fraction in the dietary treatment of phenylketonuria. Very little has been published on development of microwave formulations. Microwave cooking requires new formulation developments to obtain desired stability, texture and flavour in products. WPC may have benefits not apparent in conventionally cooked/baked formulations.

Patel et al. (1989) incorporated 10 and 18% WPC (27.41% TS) solids in buffalo milk for the manufacture of khoa, an important Indian heat-dessicated product. Greater amount of WPC produced bigger grains in khoa, which is a desirable property for preparing Kadakand- a popular khoa based Indian sweet. Addition of 5% WPC solids to cow milk improved the flavour, body and texture and colour of khoa prepared. WPC incorporated cow milk khoa compared well with the traditional buffalo milk khoa.

11. CONCLUSION

A significant increase in the production of WPC during the last three decades warrants its greater application in food products. The WPC have attracted considerable attention as functional and nutritional ingredients in a variety of food products. In particular, the functional potentiality of whey proteins for improving desired product characteristics has aroused much interest. Though soluble WPC has been found to be technical suited to a wide range of products, its use is not cost effective in all cases. More product formulation work, specially in the food industry, is needed for its effective utilisation. Because of the unique inherent properties of WPC, there lies a strong potential of its utilisation in acid foods, beverages and other new food systems.

12. REFERENCES


CLEANING OF UF/RO MEMBRANES

Dr. R. S. Patel
Dairy Technology Division, NDRI (ICAR), Karnal - 132001

1. INTRODUCTION

Like all other industrial equipment, membrane filtration plants have to be cleaned at regular intervals. The cleaning frequency varies from one application to another. The main purpose of the cleaning is to remove deposits of various kinds from the membrane surface. The material deposited on the membrane surface during operation is called fouling. The nature of the fouling will vary from one product to another. Different fouling substances have one characteristic, namely causing permeate flux to decrease in the course of time, thus reducing the capacity of the plant. For maintaining the plant capacity it is therefore of importance to keep the fouling at a minimum, which means that cleaning frequency must be adjusted to the particular product in question (Glover, 1985; Pepper and Pain, 1987 Pat et al., 1992)

2. CONSIDERATIONS BEFORE CLEANING AND DISINFECTION

Before cleaning and choice of cleaning method the following has to be considered (Kulozik and Kessler, 1985; Pepper and Pain 1987):

a) The membranes have limited resistance towards chemicals, temperature, and pressure.
b) Membrane separation characteristics (permeability) may be affected by chemicals.
c) Membranes represent a barrier for direct cleaning and disinfection on the permeate side.
d) Membrane filtration equipment can only be cleaned by CIP.
e) Application of any chemical not approved by the membrane manufacturer may cause serious membrane damage and is the user's own responsibility completely.

This statement may appear very rigorous, but so far it is our experience that deviation from prescribed rules of the game may be very expensive. Membrane damage cannot be repaired There is no way back - membranes must be replaced.

3. CLEANING OF MEMBRANE FILTRATION PLANTS: METHOD

The cleaning is CIP-wise, which means "Cleaning In Place". In fact, this means that cleaning is performed in very much the same way as ordinary production, however, with proper adjustment of the operating parameters, temperature and pressure.

In general, the cleaning will include the following points:
- Product removal from the system
- Flushing with water
- Cleaning in one or more steps, according to selected procedure
- Flushing with water
- Disinfection when a high grade bacteriological condition is required

Between each step in the cleaning procedure the plant is flushed with water

3.1 Product Removal

The product is flushed out, using water or permeate, preferably at the same temperature as that of the product. For products which tend to form gels at low temperatures this is important.

3.2. Flushing

Before the actual cleaning and between each step in the cleaning procedure the plant should be flushed. During flushing both permeate and concentrate are dumped. The flushing shall continue until a clear and neutralized flow from permeate and concentrate tubes has been obtained.

Typically, the volume for one flushing is from 3 to 5 times the internal volume of the plant.

3.3. Preparation of Chemicals And Cleaning Cycle

After displacement of product and flushing with water, the chemicals are dissolved and filled into the balanced tank. This is done while the system is under recirculating conditions which means that permeate and concentrate are recycled into the balance tank. It is important to notice that chemical in powder form should be dissolved in water before they are introduced into the system. It is always important to add the chemicals gradually to the balance tank, avoiding local over concentration of chemicals in the system. The cleaning is continued for a specified period of time under specified temperature and pressure conditions. Generally, the cleaning shall be performed under reduced pressure compared to normal operations. Typical pressures for cleaning of RO-plants are 15-20 bar and for cleaning of UF-plants 0.8-1.8 bar.

3.4. Multistep Cleaning

Some products call for several independent cleaning steps, e.g. dairy products. To accomplish a satisfactory cleaning it may be necessary to apply different chemicals in succession. This may for instance involve an acid cleaning succeeded by an alkaline cleaning containing detergents or vice versa. In such cases it is objectionable to mix chemicals from one step with the chemicals left in the system from the preceding step. Each cleaning step has to be followed by water flushing to remove impurities and used chemicals before new chemicals are put into the system. This is important (Madsen, 1972; IDF, 1979; Glover, 1985; Lefeuore, 1985).
3.5. Disinfection

Where high grade bacteriological conditions are required, as e.g for the food, dairy, and biotechnical applications, cleaning is succeeded by disinfection.

4. CLEANING CHEMICALS

4.1. Properties of Cleaning Chemicals

The cleaning of the plant has to remove the deposits and thereby restore the capacity and normal separation. For this purpose a number of chemicals can be used, and they should,

- loosen and dissolve the fouling
- keep the dirt in dispersion and solution
- avoid new fouling
- NOT attack the membrane (and other parts of the system)
- disinfect all wetted surfaces

For membrane filtration cleaning chemicals can be: (Glover 1985, Patel et al 1992).

- Caustic soda (NaOH)
- Sodium carbonate
- Phosphates
- Wetting agents
- Enzymes
- Tetrasodium EDTA
- Acids
- Chlorine compounds
- Peroxides

4.2. Water Quality

Water is the most important cleaning agent and the one used in largest quantities. Consequently, the quality of the water used is of utmost importance in order to avoid unwanted deposits originating from the water on the membranes. Specifically important is the content of deposit forming components such as iron, manganese and silicates and of course the water used for cleaning must be of good bacteriological standard. Table 1 states the required water quality for cleaning of UF and RO plants.

4.3. Selection of Proper Cleaning Chemicals

When choosing, the "right" chemical considerations must be given to the functional properties which will be most suitable for a specific applications.

The active layer of a membrane is extremely thin (approx. 1 micron), and exposure to a "wrong" chemical may prove fatal very shortly.

Today membranes are made of various polymers, each with typical resistance characteristics. Typically, polysulphone, polyamide, and cellulose acetate are used.
4.4. Ultrafiltration and Microfiltration Membranes
(GR, GRM, FS, FSM, and RC)

This group of membranes comprises the GR- and FS-types, which are made
of high resistant polymers. The RC-type is made of regenerated cellulose and limited
chemical resistance. The conditions are listed in Table 2.

5. Reverse Osmosis Membranes (HR, and HC)

This group of membranes comprises the HR-types, HR95, and HR98 as well
as type, HC50. The conditions are listed in Table 2.

Please note:
CHLORINE IS NOT TOLERATED BY HR- AND HC- MEMBRANES

6. CELLULOSE ACETATE MEMBRANE (CA)

Please note that the alkali resistance and temperature resistance are very poor.


This group of membranes comprises types of the same materials and with the
same resistance as the GR- and FS-types.

7. DISINFECTION CHEMICALS AND STORAGE CHEMICALS

In a number of applications disinfection is an essential part of the cleaning
cycle. This is particularly the case in products belonging to the food, beverage,,dairy,
and biotechnical applications.

The disinfection normally used are:

Water at 80° C (where membrane tolerance allows)
Hydrogen peroxides
Formaldehyde

Concentrations, temperature, and recycling time are given in Table 2.

When a plant is shutdown for more than approx. 40 hours, it should be
preserved (stored) in a liquid containing a chemical preventing growth of bacteria
and fungi. The chemical is recirculated 5 minutes at room temperature, before the
plant is stopped.

Before start on product, the chemical is flushed out, and a one-step-cleaning is carried
out

The chemicals used for preservations are:
Sodium bisulphite  
Formaldehyde  
Propionic acid

7.1. WARNING

Many manufacturers of formulated cleaning products offer products with the same functional properties but developed for other applications (laundry).

SUCH PRODUCTS SHOULD NOT BE USED FOR MEMBRANE FILTRATION PLANTS.

8. CONCLUSIONS

In most cases the cleaning of membrane filtration system can be accomplished by using the cleaning agents recommended by the manufacturer. The advent of high resistant UF-membranes as well as RO-membranes has in many respects made cleaning easier than before. However, a warning is necessary. Today we have a variety of membranes available with differences in chemical and temperature resistance. This means that we must keep track of what kind of membrane we use. Be particularly careful with oxidizing agents (chlorine and peroxide).

It is not possible to give complete information of all kinds of cleaning procedures at this occasion. We will, however, be at your disposal, by assisting you in solving any particular cleaning problem that might arise. Kindly contact Dr. R. S Patel, NDRI for the same.

9. REFERENCES


SIMPLE GRAPHICAL METHOD TO ESTIMATE MEMBRANE TRANSPORT PARAMETERS AND MASS TRANSFER COEFFICIENT IN A MEMBRANE CELL

Z. V. P. Murthy and Sharad K. Gupta*
Chemical Engineering Department, I.T.T., New Delhi -110 016

1. ABSTRACT

Reverse osmosis (RO) experiments are conducted in the laboratory using a cellulose acetate membrane in flat disk cell. The data are used to estimate membrane parameters and mass transfer coefficient using Kimura- Sourirajan analysis (KSA) and by a new graphical method (GM). Even though the origin of the two methods is similar, the membrane parameters and coefficients are calculated using different procedure. The parameters estimated from the KSA method, in which every parameter is estimated at each data point, are prone to experimental errors and show marked variation with operation conditions. In contrast, the graphical method, in which data at different pressures but constant feed flow rate and constant feed concentration are used in a simple graphical procedure, show that the estimated membrane parameters using reasonably constant. It is therefore shown that the estimation of parameters using the KSA method may lead to the conclusion that membrane parameters are functions of operating conditions such as pressure whereas in reality the parameters may not be functions of operating conditions at all.

2. INTRODUCTION

A reverse osmosis test cell is usually used to estimate membrane parameters and to study the concentration polarization phenomenon in reverse osmosis. The mass transfer coefficient measurements related to reverse osmosis can be divided into three main groups: (a) direct measurements using optical or microelectrode measurements (1-4), (b) indirect measurements in which the true rejection of the membrane is calculated by extrapolation to infinite feed circulation (5, 6), and (c) indirect measurements in which a concentration polarization model with a membrane transport model is used for the required calculations (7-10). All these methods have their own merits and demerits. When a two parameter model, such as the preferential sorption-capillary flow model or the solution-diffusion model, is used for describing the mass transfer inside the membrane, the estimation of membrane parameters and the mass transfer coefficient is usually carried out by Kimura-Sourirajan analysis (KSA) (9-11). In the KSA method the solute transport parameter $D_{am}/K_8$, and pure water permeability coefficient, $A$, and the mass transfer coefficient, $k$, are estimated for each and every data point, making the method laborious is proposed to estimate $D_{am}/K_8$ and $k$, while $A$ can be obtained from the slope of a plot of pure water permeability [PWP] vs applied pressure.
3. THEORY

3.1 Film Theory

To estimate the mass transfer coefficient in a reverse osmosis (RO) test cell, film theory is widely used in the literature (9-11). When a solute is rejected by the membrane, the solute concentration near the membrane surface increases. The build up in concentration at the membrane-liquid interface is termed "concentration polarization". At steady state the solute flux is constant throughout the film and equal to solute through the membrane, $N_A$. A material balance for the solute in a differential element gives

$$N_A = C_A J_v - D_A (dC_A/dx)$$

which is to be solved using the following boundary conditions:

$$C = C_{A1} \text{ at } x = 0$$

$$C = C_{A2} \text{ at } x = 1$$

where $C_{A1}$ is the solute concentration in the feed, $C_{A2}$ is the solute concentration in the boundary layer, and $l$ is the boundary layer thickness. Integration of Eq. (1) and using the above boundary conditions results in the following equation:

$$\frac{(C_{A2} - C_A)}{(C_{A1} - C_A)} = \exp (J_v k)$$

where $C_A$ is the solute concentration in the product and $k$ is the mass transfer coefficient, defined as $D_A / l$. Equation (2) can be rearranged to give a relation between the observed rejection,

$$R_0 = \frac{(C_{A1} - C_A)}{C_{A1}}$$

and the true rejection,

$$R = \frac{(C_{A2} - C_A)}{C_{A2}}$$

as

$$\ln [(1 - R_0) - \ln [(1 - R) / R]] = J_v / k$$

3.2 Kimura-Sourirajan Analysis (Ksa) Method

The KSA method (9-11) is based on a generalized capillary diffusion model for the transport of solute through the membrane. The mathematical forms of the equations are similar to those of the solution-Diffusion model though premises in their derivation are different. The working equations of KSA method are:

$$A = [PWP] / (M_B \times S \times 3600 \times P)$$

(6)
\[ N_n = A (\Delta P - \Delta \pi) \]  

(7)

\[ = C (D_{AM}/K\delta) [(1 - X_{A2})] (X_{A2} - X_{A1}) \]  

(8)

\[ = Ck (1 - X_{A1}) \ln \left[ (X_{A2} - X_{A1})/(X_{A1} - X_{A2}) \right] \]  

(9)

where \( A \) is the PWP coefficient, \( M_n \) is the molecular weight of Component B, \( S \) is the active surface area of the membrane, \( N_n \) is the solvent flux, \( C \) is the molar density of the solution, \( D_{AM}/K\delta \), and \( k \) is parameter, and \( X_{A1} \) is the mole fraction of Component A. Sourirajan and co-workers used the above equations to estimate \( A, D_{AM}/K\delta \), and \( k \) in most of their work on reverse osmosis (9-11). The value of \( A \) is first estimated from Eq. (6) from the pure water permeability data. Once \( A \) is known, then Eq. (7) is used to calculate \( X_{A2}, D_{AM}/K\delta \) and \( k \) are determined from Eqs. (8) and (9), which is the mole fraction of solute at the feed-membrane interface. Using this value of \( X_{A2}, D_{AM}/K\delta \) and \( k \) are determined from Eqs. (8) and (9).

3.3 Graphical Method

The working equations of the solution-diffusion model (12, 13) are

\[ J_v = A (\Delta P - \Delta \pi) \]  

(10)

\[ N_A = (D_{AM}/K\delta) \left( C_{A1} - C_{A2} \right) \]  

(11)

where the parameter \( A \) is same as the PWP constant and can be estimated from a plot of [PWP] vs applied pressure, and \( (D_{AM}/D\delta) \) is considered as a single parameter, namely, the solute transport parameter. Equations (10) and (11) may be combined with Eq. (4), as illustrated by Pusch (14), to give

\[ 1/R = 1 + (D_{AM}/K\delta)(1/J_v) \]  

(12)

Now, Eq. (12) can be substituted in Eq. (5) and after rearrangement it can be written as

\[ \ln \left[ (1 - R_o) \times J_v / R_o \right] = \ln \left[ D_{AM}/K\delta \right] + J_v k \]  

(13)

Equation (13) is the new working equation of combined solution-diffusion and film theory models. By using \( R_o \) and \( J_v \) data, taken at different pressures but at constant feed rate and constant feed concentration for each set, a plot of \( \ln[(1 - R_o) \times J_v / R_o] \) vs \( J_v \) will yield a straight line with a slope equal to \( 1/k \) and an intercept equal to \( D_{AM}/K\delta \).

4. THE EXPERIMENTAL PROCEDURE

Reverse osmosis (RO) experiments were performed using membranes prepared in our laboratory, in an air-conditioned room, by the phase inversion method of Manjikian (15). The composition and condition of the membranes are shown in Table 1. The reverse osmosis experimental setup is shown in Fig. 1. The RO test cell and membrane support system are shown in Fig. 2. The test cell, which is in two halves, is made of stainless steel and is fastened together with tensile bolts. The top section of the
applied pressure, as was also shown for some membranes by Pusch and Mossa (16). The separation data for a feed concentration of 6000 ppm are shown in Figs. 4 and 5

where the observed rejection, \( R_0 \), and the product flux, \( J_0 \), are plotted against the applied pressure for different feed flow rates. Other data for a feed concentration of 12,000 ppm are given in Table 2b. The membrane parameters and \( k \) are now estimated from KSA method as shown in Tables 2a and 2b. The osmosis pressures are taken from the litterature (17) for concentration range used in the experiments, and expressed by virial expansion as mentioned by Jonsson (18):

\[
\pi(X_A) = a_1X_A - a_2X_A^2 + a_3X_A^3
\]

or

\[
X_A (\pi) = b_1[\pi(X_A)] + b_2 [\pi(X_A^2)] - b_3[\pi(X_A^3)]
\]

The results in Tables 2a and 2b show that parameters \( D_{AM}/K \delta \) and \( k \) vary with the operating conditions. Although \( k \) is expected to vary with respect to the feed flow rate as well as the feed concentration, the wide variations in the values of \( D_{AM}/K \delta \) is unexpected. Estimation of each parameter for every pressure may not be required, and \( k \), which is a function of feed flow rate, cell geometry, and solute system, varies with pressure in this analysis.

The same data are now used to calculated parameters for the graphical method (GM) proposed earlier. In the GM method, data taken at different pressures while keeping the other operating variables constant, such as the feed concentration and the feed rate, form a single set used to estimate the parameters \( D_{AM}/K \delta \) and \( k \). Plots of in \([(1 - R_0) X J_0/R_0] vs J_0 \) were prepared as shown in Figs. 6 and 7. The excellent straight line fit of the experimental data clearly shows that the membrane parameters and mass transfer coefficient are independent of applied pressure. The parameters estimated from the GM method are given in Table 3. It can be observed that the parameter \( D_{AM}/K \delta \) is nearly constant for the range of experimental data studied and that \( k \) varies with the feed rate.

Apart from our data, published data (Table 4) of Rosenbaum and Sikiens (19) was used to verify the KSA and graphical methods. Parameters for these data calculated from the KSA method are shown in Table 4, and the same data were analyzed by the graphical method as shown in Table 5.

If we compare the values in Tables 2a, 2b, 3, 4, and 5, we not only find substantial differences in the values of \( D_{AM}/K \delta \) but also marked differences in the values of \( k \), even for the same feed flow rate.

The main problem of the KSA method is that the value of the mole fraction at the feed-membrane interface, \( X_A2 \), needs to be indirectly calculated from Equ. (7), i.e.,
cell is the high pressure side flow distribution chamber and the bottom section, which is lower pressure side, is used as the membrane support system. The support arrangement provides sufficient mechanical support for test membrane pressures up to 110 atm or more. The active membrane surface area is 60 cm².

**TABLE 1. Composition and Conditions of Membrane**

<table>
<thead>
<tr>
<th>Composition wt%</th>
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</tr>
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<tbody>
<tr>
<td>Cellulose acetate (E-398-3)</td>
<td>15</td>
</tr>
<tr>
<td>Dioxane</td>
<td>40</td>
</tr>
<tr>
<td>Acetone</td>
<td>10</td>
</tr>
<tr>
<td>Maleic naphydrde</td>
<td>5</td>
</tr>
<tr>
<td>Methanol</td>
<td>25</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5</td>
</tr>
</tbody>
</table>

**Conditions:**
- Wet membrane thickness, mm: 0.25
- Evaporation time, m: 1
- Gelation time in 0-3°C water, hours: >1
- Annealing temperature, °C: 90
- Annealing time, m: 10

---

Pressure pretreatment given at 50 atm overnight and at 110 atm for about 3 hours. LR grade chemicals (merck).

To avoid membrane compaction during the separation process, the membrane is first pretreated overnight at 50 atm and then for about 3 hours at 110 atm with distilled water. The pure water permeability [PWP] is measured at different operating pressures. A sodium chloride-water system is used to get separation data in the concentration range from 6000 to 12,000 ppm. The brine feed solutions (about 12 L) are prepared by taking a calculated quantity of NaCl and dissolving it in distilled water. After pumping the feed solution to the storage tank, nitrogen gas is used for the initial pressure buildup and then the system is initially operated for about 2 hours to reach steady-state. The operating pressure is controlled with a pressure regulating valve. To measure the flux rate and concentration, two samples of permeate solution are collected over 4 minutes for every set of reading at a certain pressure. The feed and product samples are analyzed by the conductivity method (Global Electronics, Hyderabad) at 25°C. The feed rate is varied between 300 and 1500 ml/ min, and the operating pressure is varied from 20 to 100 atm.

5. **RESULTS AND DISCUSSION**

The pure water permeability [PWP] data are shown in Fig. 3. The slope of the straight line, which is the PWP constant A, is 1.4904 X 10⁻⁴ cm/s. It is seen from Fig. 3 that A of the membrane used in the present work shows no dependence on the
<table>
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<th>Set</th>
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\[
\pi(X_{A2}) = \Delta P + \pi(X_{A1}) - N_B / A
\]  \hspace{1cm} (16)

Once \(\pi(X_{A2})\) is known, Eq. (15) is used to determine \(X_{A2}\). Or, the calculation of \(X_{A2}\) requires the following experimentally measured quantities: \(\Delta P\), \(X_{A1}\), \(N_B\), and [PWP] data. Any errors in the measurement of these quantities adds up to give a large
error in the values of $X_{AD}$, and then errors are further propagated in the calculation of $D_{AM}/K\delta$ and $k$.

**TABLE 4. Parameters Calculated Using Rosenbaum and Skiers Data [19] by the KSA Method:**

<table>
<thead>
<tr>
<th>Set</th>
<th>$\Delta P$ (atm)</th>
<th>$A \times 10^4$ (g/mol/cm$^2$.s.atm)</th>
<th>$R_0$</th>
<th>$N_p \times 10^7$ (g/mol/cm$^2$.s)</th>
<th>$k \times 10^6$ (cm/s)</th>
<th>$(D_{AM}/K\delta) \times 10^6$ (cm/s)</th>
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**TABLE 5. Parameters Calculated Using Rosenbaum and Skiers Data [19] by the Graphical Method**

<table>
<thead>
<tr>
<th>Set</th>
<th>$k \times 16$ (cm/s)</th>
<th>$(D_{AM}/K\delta) \times 10^6$ (cm/s)</th>
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**6. CONCLUSION**

The KSA method used in the literature is time-consuming and labourious, and the calculated parameters may show variation with operating conditions. In this present work the equations of solution-diffusion model and the film theory model are rearranged so that they can be used to estimate the membrane parameters $D_{AM}/K\delta$ and $k$ simultaneously by a simple graphical method. The data obtained in our laboratory show that the membrane parameters found by using the GM method are essentially constant in the range of experimental data collected while the same data when analyzed by using the KSA method show marked-variation in membrane parameters under different operating conditions.
7. NOTATIONS

$ai$ virial coefficients in Eq. (14)
$ai$ virial coefficients in Eq. (15)
$A$ PWP constant (kmol/m².kPa or m/s/kPa)
$C$ molar density of the solution (kmol/m³)
$C_{ui}$ molar concentration of component $i$ in phase $j$ (kmol/m³)
$D_{AM}/K_d$ solute transport parameter (m/s)
$D_u$ diffusivity of component $i$ in component $j$ (m²)
$I_v$ solvent volume flux (m³/m².s)
$k$ mass transfer coefficient (m/s)
$l$ thickness of the concentration boundary layer (m)
$N_i$ molar flux of component $i$ (kmol/m².s)
$\Delta P$ pressure difference across the membrane (kPa)
$R$ true rejection
$R_o$ observed rejection
$x$ coordinate direction perpendicular to the membrane (m)
$\Delta x$ membrane thickness (m)

Greek Symbols

$\delta$ effective thickness of a membrane (m)
$\Delta \pi$ osmotic pressure difference across the membrane (kPa)

Subscripts

A solute
B solvent
M membrane
1 seed solution
2 boundary layer solution
3 permeate solution

8. REFERENCES

**FIG. 1** Reverse osmosis experimental setup.

**FIG. 2** Reverse osmosis test cell.
FIG. 3 The effect of applied pressure on [PWP].

FIG. 4 The effect of applied pressure on observed rejection with different feed rates (6000 ppm NaCl–water feed).
**FIG. 5** The effect of applied pressure on product flux with different feed rates (6000 ppm NaCl–water feed).

**FIG. 6** Plot of ln\([1 - R_a]/J_0\) vs \(J_0\) for 6000 ppm NaCl–water feed and 300 mL/m and 1500 mL/m feed rates.
FIG. 7  Plot of $\ln(1 - R_o) J_o / R_o$ vs $J_o$ for 12,000 ppm NaCl-water feed and 300 mL/m and 1500 mL/m feed rates.

FIG. 8  Plot of $\ln(1 - R_o) J_o / R_o$ vs $J_o$ for 0.01 M and 0.1 M NaCl-water feed solution [Data of Rosenbaum and Sikes (19)].
Application of Membranes in Biotechnology

by

G.P. Agarwal
Department of Biochemical Engineering & Biotechnology
Indian Institute of Technology
Hauz Khas, New Delhi-110 016.

Membranes have already become an integral part of many processing industries as a separation tool, yet its potential is not fully explored. With the development of the first asymmetric membrane about three and half decades ago, expectations of all processing industries literally rose sky high. The switch over from existing separation processes to membrane based separation processes (MBSP) was considered a mere formality. However, some of these expectations were not met commercially because of continued high cost of membranes and modules especially in Indian context.

With the increased awareness of the potential of MBSPs, its application in biotechnology is going to gain increasing share in future. New membranes and modules have been developed in recent years which would reduce membrane fouling and concentration polarization, the two main limitations of MBSPs application in biotechnology. Biotechnology is a glamorous description of a wide range of products derived from biological agents. It most frequently refers to the genetic manipulation of microorganisms such as yeasts, bacteria and fungi. The euphoria associated with the widespread rush into biotechnology by corporate world has abated with the realization that successful commercial exploitation of the new
"biotechnology" will be limited not by the microbiology or genetic engineering per se but by the downstream processing (i.e. the separation and purification of the product). Fermentation broths tend to be very dilute and contain complex mixture of compounds. In addition they are highly impure and sensitive to almost any extremes of operating parameters normally used in conventional separation processes. The major applications of MBSPs, microfiltration and ultrafiltration are in the areas of:

- Separation and harvesting of enzymes and microorganisms.
- Concentration of dilute solutions of proteins.
- Removal of salt from the complex mixture.
- Fractionation of proteins.
- Continuous high performance bioreactors for enzymatic and microbial conversion processes.
- Production of pure, high quality water.

Application of microfiltration and ultrafiltration in above areas will be briefly described and the potential for some more important processes will be highlighted in the present lecture.

REFERENCES: