Particle migration effects as a basis for effective microfiltration

August 27, 2014: Karin Schroën, Anna van Dinther, Remko Boom
Overview

- Fractionation / separation of components
  Dairy as an example: principle mechanisms

- Particle migration phenomena
  - Simulations
  - CSLM
  - Membranes (low, high concentration, actual food)

- Process design
Milk fractionation

- Increased shelf life
- ‘Fresher’ products (cold sterilisation)
- Less transport costs
- Better defined starting materials
- New products

➢ Other processes
Fractionation of milk

- Starting point:
  - Size-selective particle separation
  - Membranes

Fractionation of milk

- So we are trying to separate this with this!
Surprisingly: sometimes it works!

Cold sterilisation
Separation of milk fat from milk
Concentration of casein
Recovery of serum protein from whey

But not complete fractionation!
# Cold sterilisation

<table>
<thead>
<tr>
<th>Membrane type and flux</th>
<th>Process conditions</th>
<th>Log reduction</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic 1.4 μm; 1.4•10^{-4} m/s</td>
<td>cross flow / pressure, UTP, back pulsing</td>
<td>above 3.5</td>
<td>Saboya and Maubois 2000 Lait</td>
</tr>
<tr>
<td>Reversed asymmetric 0.87 μm; 1.4•10^{-4} m/s</td>
<td>0.5-1 m/s; back pulsing 0.2-1 s^{-1}</td>
<td>between 4 and 5</td>
<td>Guerra et al. 1997 Int. Dairy Journal,</td>
</tr>
<tr>
<td>Microsieve 0.5 μm</td>
<td>dead-end filtration of spiked SMUF</td>
<td>6.6</td>
<td>Van Rijn and Kromkamp (patent)</td>
</tr>
<tr>
<td>Bactocatch: ceramic membranes</td>
<td>6 to 8 m/s</td>
<td></td>
<td>Holm et al. (patent)</td>
</tr>
</tbody>
</table>
# Concentration of casein

<table>
<thead>
<tr>
<th>Membrane type and flux</th>
<th>Process conditions and flux</th>
<th>Concentration factor</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceraflo 0.22 μm; 2.5•10^{-5} m/s</td>
<td>6.9 m/s; 190 kPa</td>
<td>3</td>
<td>Pouliot et al. 1996 Int. Dairy J.</td>
</tr>
<tr>
<td>Membralox 0.2 μm 1.9•10^{-5} - 1.3•10^{-5} m/s</td>
<td>7.2 m/s; 193 kPa</td>
<td>2-10</td>
<td>Vadi and Rizvi 2001 JMS</td>
</tr>
<tr>
<td>Ceramem asymmetric 0.05 μm; 3.1•10^{-5} m/s</td>
<td>5.4 m/s; 138 kPa</td>
<td>2</td>
<td>Punidadesas and Rizvi 1999 Food Res. Int</td>
</tr>
<tr>
<td>Membralox 0.1 μm; 9.7•10^{-5} - 2.5•10^{-4} m/s</td>
<td>0.45 m/s; 34 kPa turbulence promoters 12.5 m/s; 65 kPa</td>
<td>1</td>
<td>Krstic et al. 2002 JMS</td>
</tr>
</tbody>
</table>
Surprisingly: sometimes this works!

A lot of measures are taken to keep the process running

- Back pulsing / shocking (very frequent)
- Turbulence promoters
- Critical flux concept
- Uniform transmembrane pressure concept
- (acoustic waves, sonication)

➤ And lots of cleaning!
Is there any rationale behind this?

‘Any measure that gets rid of accumulated particles is good.’

But is this the ‘best’ approach?

- Focus on particles (starting point of our research)
- Focus on membrane and module design
Critical flux: starting point ‘particles’

Transmembrane flux (m/s)

Trans membrane pressure (Pa)

I

II

III

$J_{\text{crit}}$

$P_{\text{crit}}$

Trans membrane pressure (Pa)
Critical flux: starting point 'particles'

Transmembrane flux (m/s)

Transmembrane pressure (Pa)

Delicate balance: flux ~ diffusion
Critical flux: starting point ‘particles’

Transmembrane flux (m/s) vs. Trans membrane pressure (Pa)

I  II  III

$J_{\text{crit}}$  $P_{\text{crit}}$

Back diffusion ($\Delta C$)

Flux ($\Delta P$)

flux > diffusion
Critical flux: starting point ‘particles’

Transmembrane flux (m/s)

Transmembrane pressure (Pa)

Flux ($\Delta P$)

Back diffusion ($\Delta C$)

$J_{\text{crit}}$ $P_{\text{crit}}$

flux $\gg\gg>>$ diffusion

Critical flux: starting point ‘particles’
Rationale for particles

Balance flux and back transport mechanism!

Particles of different sizes in milk

- Shear induced diffusion

UTP concept makes use of this, but can we do better?

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R.H. Davis, Separation and Purification Methods, 21, 1992
Intermezzo: issues membrane design

- Pore size distributions!
  - Local fluxes differ
  - Length of module
  - How to design a process?

- Membranes with uniform pores

- Prerequisite: Surface properties
  - Adhesion/binding to the surface
Membrane design: Pore size distribution

Polymeric membrane (poly-sulfone)

Micro sieve
Circular pores

Micro sieve
Slit shaped pores

Ceramic membrane

Metal sieve
Slit shaped pores
Membrane design: Pore geometry

- Resulting force on a particle (drag, pressure, flow)

**TMP: 3.33 kPa; Particles 1.2 µm on 1 µm pore**
Membrane design: Surface properties

- Uniform pore size
  - High fluxes (but also high accumulation rate!)
  - Pore design & removal particles

- Surface properties
  - Mild modification
  - Length of molecule
  - Covalent bond

\[
\text{CH}_3
\]

Back to the main issue

Prerequisites

- Pore size design
- Surface modification
- Uniform pores

Core of the design

- *Particle interaction in close proximity to the membrane*

Simulations as tools → experimental validation
Back to particle behaviour

- Limiting process is concentration polarisation
- Simulation tools to predict behaviour (in complex feeds)
Simulation of shear-induced self-diffusion

- Lattice Boltzmann method
- Suspension flow (Ladd, 1994)
- CFD-type approach
- Hydrodynamic interactions fully resolved
- Suspension particles considered as hard spheres
- 2-D simulations

Mean square displacement: mono-dispersed

Shear-induced diffusion: mono-disperse

Shear induced diffusion strong function of concentration

$$D_{\text{shear}} = \frac{1}{3} \gamma a^2 \varphi^2 (1 + 0.5e^{8.8\varphi})$$
Shear-induced diffusion: bi-disperse

Large particles dominate migration behaviour

Surprising flux behaviour

- Small particles dominate flux
- Shear induced diffusion simulations point to reverse

Kromkamp et al, Desalination (2002) 146, 63-68
Particle deposition

- **So what is happening?**

*Red large particles 9.7 µm (97.5%); Green small particles 1.6 µm (2.5%)*

*Membrane cut off 100 kDa, overlays of CSLM images*

Kromkamp et al, 2006, Journal of Membrane Science
Relative amount small particles in cake

Large particles 9.7 µm; Small particles 1.6 µm

Kromkamp et al, 2006, Journal of Membrane Science
Hypothesis: Shear induced diffusion can lead to enrichment of small particles and depletion of large particles near membrane!

Would confirm deposition & cake layer formation dominated by the small particles

Kromkamp et al, 2006, Journal of Membrane Science
CSLM: effect of concentration

- Quantify effects
  - CSLM in closed microchannel
  - Shear-induced diffusion only!

\[ D_{shear} = \frac{1}{3} \gamma a^2 \varphi^2 (1 + 0.5e^{8.8\varphi}) \]

Concentration 2.65 \mu m particles in channel of 100 \mu m:

\( \varphi_{tot} \) is 0.38 (○), 0.19 (▲), 0.09(□)

\( v \) is 20.8 \mu m/s

CSLM: effect of particle size

- Quantify effects
  - CSLM in closed microchannel
  - Shear-induced diffusion only!

\[
D_{\text{shear}} = \frac{1}{3} \gamma a^2 \varphi^2 (1 + 0.5e^{8.8\varphi})
\]

Concentration large & small particles in channel of 100 μm:

- \( \varphi_{\text{tot}} \) is 0.38
- (○) particles 1.53 μm
- (▲) particles 2.65 μm
- \( v \) is 20.8 μm/s
- \( \varphi_{\text{small}}/\varphi_{\text{total}} \) is 0.5

Membrane fractionation (high concentrations)

- Quantify effect on emulsions
  - 20 μm pore size, metal sieve
  - channel height 200 micron

Emulsions:
Small 1.35 μm,
Large 2.66 μm
φ_{tot} is 0.27
φ_{S}/φ_{tot} is 0.50
v is 0.59 m/s
Flux: 200-2200 L/m²·h

Membrane pore >> droplet, no accumulation
Balance particle transfer to membrane and back diffusion
A closer look at fractionation

- Depending on cross-flow versus trans-membrane velocity
  - Only small particles in permeate
  - Sometimes at higher concentration than in the feed!

Volume fraction 0.37
Small 1.35 μm,
Large 2.66 μm
φ_S/φ_tot is 0.50

van Dinther et al, Innovative Food Science and Emerging Technologies 18 (2013) 177–182
Effect of concentration

Higher concentration works better, till certain limit!
Shear induced diffusion is more pronounced
Membrane fractionation (low concentration)

- Various metal sieves

- **Skimming**: Only small particles in permeate

Membrane fractionation of milk fat

- Pore size 5 μm
- Deposit free operation
- CFV and flux determine composition of permeate
- Pore size not so relevant

Option: pore size > largest particle

Fractionation with large(r) pores

➢ Opportunities: ‘only’ process control is needed!
Conclusions / implication process design

- Detailed investigations into particle behaviour:
  - Diffusion highly concentration dependent
  - Large particles dominate diffusive behaviour
  - Smallest particles dominate flux behaviour (depending on pore size)
  - Large pores: Selectivity dependents on process conditions

- Processes could be controlled through cross flow and pressure
  - Choice of pore size may be not too important....
  - Fouling could be better controlled
  - High fluxes are possible during continuous operation
What is needed to get this to work?

- Entrance length for sufficient migration (1 mm - 50 cm)
- Large uniform pores >> particles
- Process conditions chosen based on
  - Diluted systems → fluid skimming
  - Concentrated systems → shear induced diffusion
- High fluxes and no fouling
- Yeast, emulsions, algae, gel beads: Principle works!
- Fractionation of particles very close in sizes possible
Thank you for your attention

Pore size may not always be that relevant.....but process conditions are

Micrometer scale insights are needed for radically new process designs

Keep looking for unexpected options!

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