Silica stabilisers and filtration

Sonya Broderick, PQ Silicas
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Introduction
Silica & stabilisation.
Overview of silica and the brewing process

Silica is a process aid used to deliver colloidal stability to beer.

This is achieved through the selective removal of haze sensitive proteins.

The silica adsorbs haze sensitive proteins and when the silica is removed either by sedimentation in MV or through capture on the filter the haze sensitive protein is removed also.

Silicas are a proven & reliable stabiliser within the brewing industry.
Protein-Polyphenol Haze Formation

Polyphenol + Protein + H$_2$O

$\text{(Polyphenol)}^n(\text{Protein})^m + \text{H}_2\text{O}$

soluble complex

Low T, 0 degC
Redissolves at high T

$\text{(Polyphenol)}^a(\text{Protein})^b + \text{H}_2\text{O}$

ChillHaze:
Reversible association between polyphenol and protein.

0.1 to 1.0 micron

$\text{(Polyphenol*)}^y(\text{Protein*})^x + \text{H}_2\text{O}$

Precipitation
Oxygen, metal ions

Permanent Haze:
Aged complex - stable form.

1.0 to 10.0 microns
Haze protein characteristics

- Mw. 16.6 kD and 31.1 kD
- High in proline
- Originates from malt
Haze-forming (tannoid) polyphenols

Flavanoid skeleton

Tannoids Mw <2kD

The general structure of a homologous procyanidin is 4→8 bonded, though there can be 4→6 branch points, and a gallic acid esterified at the 3 position.
Silica mode of action

- The silica delivers stability through the adsorption of the proline rich haze sensitive proteins.
- If the haze sensitive protein content is removed or sufficiently reduced then haze forming tannoid interaction is prevented.
- Result: Colloidal stability
Brewing Silicas
Silica Gel Production

Sodium Silicate

Sulphuric Acid

Hydrosol

Hydrogel

Polysilicic acid unit

Milled Hydrogel

Wash Mill

Wash/age Dry

Xerogels
Brewing Silicas: Important properties

- Silica gel used in the brewing process is amorphous, non-crystalline inert material.
- It is a porous material
- The key properties for protein removal are the no. of silanol groups and the pore size.
Amorphous Silica structure

- Primary silica particle aggregate ca. 15Å diameter
- Secondary silica particle aggregate ca. 120Å diameter
- Tertiary silica particle aggregate ca. 10 µ diameter

Fracture line
Silica pore size and protein uptake

Protein Uptake ( % )

Average Pore Diameter ( Angstroms )
Silica surface chemistry

Free H$_2$O

5 Layers free water

3 Layers adsorbed water

OH OH

OH OH OH

OH OH OH OH OH OH

Surface Area (hydrated)

Surface Area (dried)

Pore (dried)

Pore (hydrated)
Brewing Silicas

- **Hydrogel: 65% moisture**
  - Quick dispersing
  - Fast settling for in-tank application
  - Permeability control for application at the filter

- **Modified hydrogels: 30-35% moisture**
  - Free flowing
  - High protein adsorption capacity
  - Fast settling

- **Xerogels: < 10% moisture**
  - High adsorption capacity
  - Adsorption robust to temperature increase
  - Permeability control for application at the filter

Increasing effectiveness
Filtration
Filtration

- Filtration is a separating technique of two phases, one is solid, the other is liquid.

  Passing through a porous medium, the solid phase is retained, the liquid phase is clarified.

  The purpose of the operation is purification and clarification of a liquid.
Types of Filtration

• Traditional filtration
  – Dead end
  – Kieselguhr
    • Candle filters
    • Leaf filters
    • Plate and frame filters

• Crossflow membrane filtration
  – Continuous flow
  – No Kieselguhr
    – CMF - centrifuge
      (Profi system)
    – CMF - no centrifuge
      (Norit system)
Traditional Filtration
Traditional Filtration

• Dead end filtration
  – Precoats
    • Protect the filter septum from the suspended solids and to ensure even flow of the liquid phase.
    • 1st precoat normally perlite or a perlite/cellulose blend
    • 2nd precoat dictates the level of filtration/polishing that is achievable.
  – Bodyfeed
    • Bodyfeeding is used to stop suspended particles from blinding the precoats. Ideally the bodyfeed should be of similar particle size and range as the particles to be removed, this will allow for the filter cake to build up during filtration run whilst retaining a porous, stable and non-compressible cake, increasing the filter run length and reducing the pressure drop.
‘BARRIER’ SYSTEM

finer second precoat

small particles caught at interface
Filtration Principles

- Process and design of filtration equipment is governed by Darcy’s equation

\[ \Delta P = \mu . u . l \frac{\beta}{\beta} \]  

(equation 1)

where,  
\( \mu \) = beer viscosity (typically 3 cP or 3 mPa.s at 0°C)  
\( u \) = Hydraulic loading (flow rate per unit area, m³/m².s)  
\( l \) = filter cake bed depth, m  
\( \Delta P \) = pressure drop, Pa
Filtration Principles - Plate and Frame or Leaf filters

• For plate and frame and leaf filters, filter cake depth is given by:

\[ l = \frac{t \cdot u \cdot c}{\rho} \]  

(equation 2)

where, 
\( c = \) filter aid addition, kg/m\(^3\)
\( \rho = \) filter cake density, kg/m\(^3\)
\( t = \) filtration time, h.

As filtration progresses bed depth increases linearly and as equation 1 shows pressure increases proportionally.
Filtration Principles - Candle Filters

- For candle filters the same principles apply, except as filtration progresses the area of the filter cake surface expands.

At $t_0$, surface area per unit length of candle = $2\pi r_0 \text{ (m}^2/\text{m})$
At $t_1$, area = $2\pi r_1 \text{ (m}^2/\text{m})$

The rate of bed build up can be derived from:

$$ r = \frac{t \cdot q \cdot c}{2\pi r \cdot L} \quad \text{(equation 3)} $$

where, $(q/2\pi r \cdot L) = \text{flow per unit area per unit length of candle}$

Because of this effect, the optimum flow rate per nominal unit area of clean candle will be greater than for a filter of constant area.
Filter Performance - Plate & Frame or Leaf versus Candle

The difference in rate of cake build-up means candle filters are able to maintain flow rate for longer periods.

<table>
<thead>
<tr>
<th>Low Permeability Filter Cake (0.01 Darcy)</th>
<th>Filtration period (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Plate-Frame or Leaf (hl/m².h)</td>
<td>7.2</td>
</tr>
<tr>
<td>Candle (hl/m².h)</td>
<td>8.3</td>
</tr>
</tbody>
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<table>
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<tr>
<th>Low Permeability Filter Cake (0.05 Darcy)</th>
<th>Filtration period (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Plate-Frame or Leaf (hl/m².h)</td>
<td>16.2</td>
</tr>
<tr>
<td>Candle (hl/m².h)</td>
<td>21.6</td>
</tr>
</tbody>
</table>
Filter Performance

- Filter aid and silica gel stabilisers form an incompressible filter cake with beer solids such as yeast, protein and carbohydrate.
- The filter cake increases with time until at some point it fills the filter.
- The rate of accumulation of the cake depends upon the beer loading and solids content. This in turn determines the amount of bodyfeed required.
- Filter design is a compromise between flow loading, rate of accumulation, final allowable cake depth, maximum pressure and plant costs.
- Optimum filter operation is achieved through achieving the correct balance between solids loading and differential pressure.
Filter Performance

- The maximum differential pressure for most equipment is in the region of 6 bar (600 kPa). Typical beer viscosity at a filtration temperature of 0°C is 3 cP (3 mPa.s).

- The permeability of a typical bodyfeed filter aid, operating at close to the optimum level of beer solids, will typically be in the range of $1 \times 10^{-14}$ to $5 \times 10^{-14}$ (0.01 to 0.05 Darcies).

- In practice therefore it is useful to consider reducing filter aid proportionally with silica gel addition. This will maintain the solid loading on the filter.

- In practice candle filters can maintain a higher loading than plate and frame filters and leaf filter.
Traditional Filtration - Silica Choice

- Choice of stabiliser must not impact on filtration performance
- Permeability
  - the permeability of the silica must compliment that of the bodyfeed regime.
  - Different permeability grades available
    - Xerogels : - XLC, XLC 6, XLC Turbo, L10
    - Hydrogels :- Standard, PC5, PC6, QD7
    - Semi-hydrogels :- PCSX, PC9

- Silica removed as part of filter cake.
Traditional Filtration - Silica Choice

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  - Silica removed as part of filter cake.
**Traditional Filtration**

- The permeability of the silica is controlled through the particle size distribution (psd) and also the particle size.

- A narrower distribution will create a more permeable silica.
- If the psd consists of smaller particles it may result in bed packing of the filter and cause $\Delta P$ to rise sharply.

- If the psd is of the same range but consists of larger particles it will maintain flow rate but there may be a reduction in stabilisation performance due to resultant lower surface area presented.
  - This could result in a higher loading of silica being required but also a corresponding reduction in filter aid to maintain solid loading on the filter.
Traditional Filtration

Higher fines content may increase bed packing.

Narrow psd distribution but increased permeability but does it compliment the filter regime?

Impact on stabilisation and therefore dosage rate and Bodyfeed implications to be considered.
Crossflow Membrane Filtration
Crossflow Membrane Filtration

- Key difference between DE filtration and CMF filtration is that in CMF there is no filter bed formation.
- Traditional measures of silica powder permeability are therefore less important.
Crossflow Membrane Filtration Systems

- **Type 1**
  
  Solids are sent with the beer to the filter.  
  e.g. Norit system

- **Type 2**
  
  Centrifuge present to remove solids prior to beer reaching membrane  
  e.g. Profi system (Pall Seitz / Schenk)
Crossflow Membrane Filtration

• **Crossflow filtration** removes any remaining yeast and insolubles from the beer to achieve brilliant clarity. Its function is the same as a traditional filter but it is does not use DE.

• The potential downside associated with CMF is loss in throughput due to membrane fouling.
  • Membrane fouling can be attributed to yeast cells, protein-tannin complexes, stabilisation products and hop resins.
Crossflow Membrane Filtration

- **What is the solution?**
  - Minimise membrane fouling & maintain porosity.

- **How can silica stabilisation management help deliver the solution?**
  - Particle size distribution controlled silicas can help maintain porosity at the filter and also prevent fouling due to minimum amount of fines present.
  - Fast settling hydrogels employed in maturation will prevent carry over of solids to either the centrifuge or the filter.
  - Particle size distribution controlled hydrogels and xerogels contain a minimum amount of fines. Therefore more easily removed by centrifugation.
## Crossflow Membrane Filtration

<table>
<thead>
<tr>
<th>Product</th>
<th>Characteristics</th>
<th>Benefits</th>
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<tbody>
<tr>
<td>PC5 hydrogel</td>
<td>PSD controlled - minimum fines</td>
<td>Settles quickly &amp; fully in MV. Easily removed by centrifugation. Minimum membrane fouling</td>
</tr>
<tr>
<td>XLC xerogel</td>
<td>PSD controlled - minimum fines</td>
<td>Easily removed by centrifugation. Minimum membrane fouling.</td>
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Crossflow Membrane Filtration Systems

• **Benefit to Type 1 CMF system**
  
  Employment of particle size distribution controlled stabilisation products to minimise impact if membrane fouling occurs.
  
  • Lucilite PC5 and Lucilite XLC proven to work in such a system

• **Benefit to Type 2 CMF system**

  Employment of particle size distribution controlled stabilisation products dosed prior to centrifugation to minimise carryover but also to prevent membrane fouling in the event of carryover..
New Development
New Development for CMF

• **XLC Turbo**
  – Is a new product developed especially with Crossflow membrane systems in mind.
  – Tailored PSD, designed for maximum benefits on CMF systems whilst maintaining stability performance.
    • Further reduction in fines and larger average particle size.

• **Benefits**
  – Type 1 :- will further reduce membrane fouling allowing for longer filtration runs between backflushes.
  – Type 2 :- tailored PSD allowing for improved removal by centrifuge, therefore further minimising carryover and also resulting in the reduction of membrane fouling allowing for longer filtration runs between backflushes.
New Development for CMF

- XLC Turbo
  - Currently undergoing brewery production trials
  - Pilot scale trials suggest an increased efficiency of 20% longer runs between backflushes.
Summary

- Brewing silicas adsorb haze sensitive proteins.
- The silica and the adsorbed proteins are then removed either by sedimentation in MV or through capture on the filter.
- There are two main filtration technologies, traditional dead end and the newer technology of crossflow membrane filtration.
- Compatible silicas are available for use with both types.
- New filtration technology has resulted in the demand for products with improved compatibility.
- PQ endeavour to continue to meet the needs of our customers as technology evolution dictates.