WEBINAR:
Silica Gel for Beer Stabilization

6th December

PQ Corporation

BRITESORB
BEER STABILIZERS

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Presentation Overview

- Beer stabilization
- Practical aspects of using silica gel
- Gluten Free Beer
- Organic Beer
- Crossflow Membrane Filtration

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Beer stabilization

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Colloidal Stability

- **Colloidal stability** is related to the tendency to form non-biological haze due to interactions between beer components, mainly polyphenols and proteins, leading to the formation of visible precipitates.
  - affects the shelf life of the beer
  - high colloidal stability = long shelf-life

- Interaction between haze forming (*sensitive)* proteins and haze forming (*tannoid)* polyphenols forms a visible colloidal haze that limits shelf life

- Haze components from malt (proteins, polyphenols) and hops (proteins, polyphenols)

- **Beer haze composition:**

  40-75% proteins
  ~17% polyphenols
  3-13% carbohydrates
  0.7-5.0% ash
  Traces of Cu, Fe, Al

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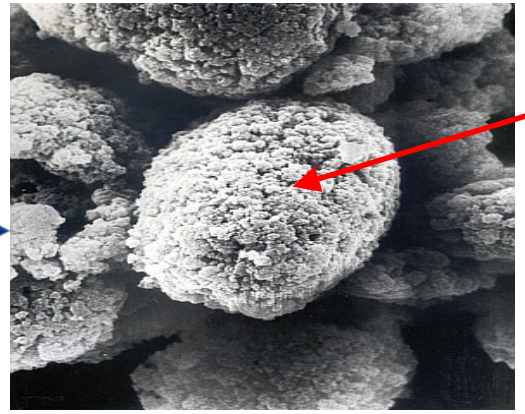
Stabilizers

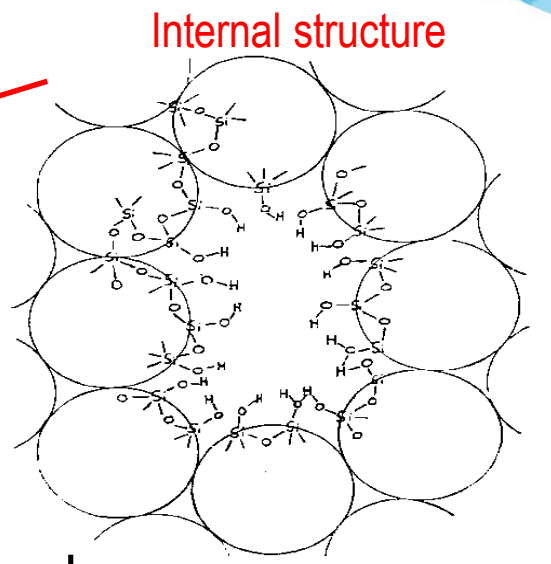
Stabilizer	Target	Process	Comment
Silica gel	proteins	adsorption	selective to hydrophilic haze proteins
Proteolytic Enzyme	proteins	degradation	poor foam retention, GMO based, still present and partially active in final product
Tannic Acid / Gallotannins	proteins	Precipitation	voluminous sediment in tank, less effective (higher dosage needed) with impact on colour, foam and flavour, present in final product
PVPP	polyphenols	adsorption	more expensive than silica, impact on long term flavour stability (lower anti-oxidant potential)

From Sand to Porous Silica

SAND



POROUS SILICA



natural product
no porosity
no adsorptive properties
high quality
low metals content

- synthetic amorphous powder
- high purity, low metals
- internal porosity (sponge-like)
- very high surface area (> 400 m^2/g)
- contains reactive silanol (Si-OH) groups
- selectively removes haze-forming proteins
- controlled particle size distribution
- process aid

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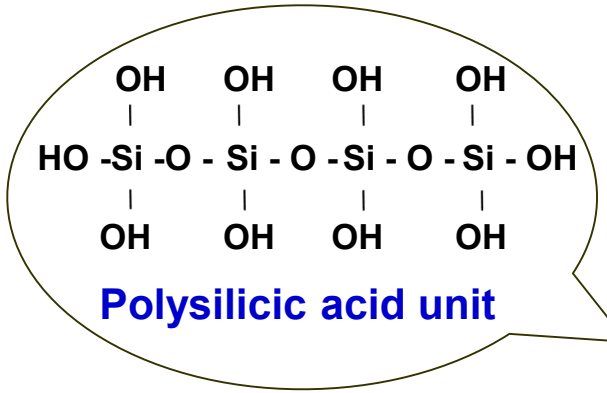
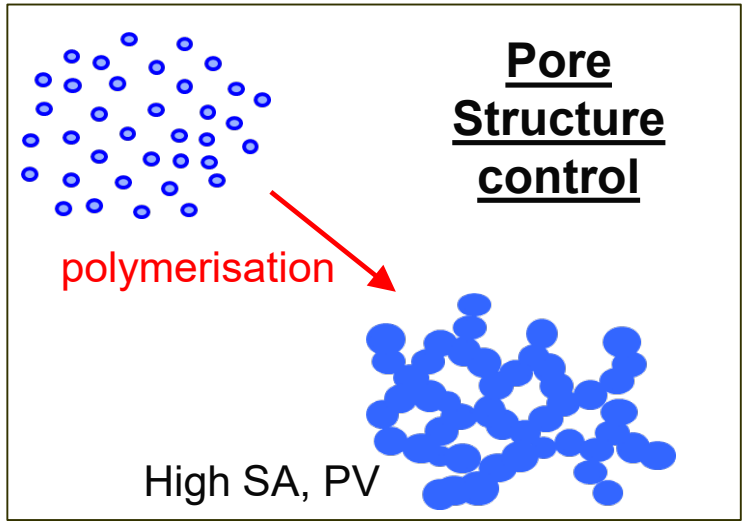
BRITESORB® Silica Gel Production

Sodium Silicate

Mineral Acid



Hydrosol



BRITESORB® Xerogels

Wash/age

Dry/mill

Hydrogel

Wash

Mill

BRITESORB® Hydrogels

BRITESORB BEER STABILIZERS - produced from PQ's own high purity sodium silicate

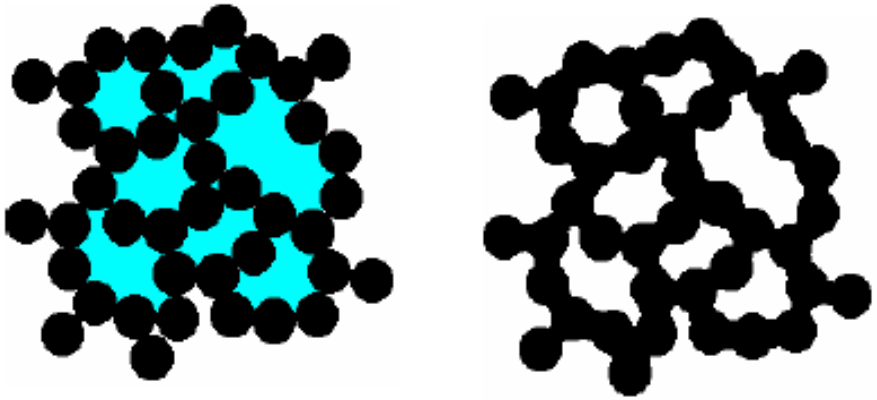
Two main types of Silica Gel

Hydrogel

A form of silica gel in which the pores are filled with water

Xerogel

A dried form of silica gel



Hydrogel Xerogel

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Britesorb Silica Gels

Increasing effectiveness

Increasing solids content

Decreasing dosage

Hydrogel: 35% solids

- Non-dusty, free flowing powders
- Quick dispersing in water
- Fast settling for in-tank application
- Highest permeability

Hydrated Xerogel: 65% solids

- Non-dusty, free flowing powder
- Higher protein adsorption capacity
- Fast settling for use in-tank
- Good filtration performance

Xerogel: >90% solids

- Highest adsorption capacity
- Fast adsorption
- Can be used either in-tank or at the filter

Increasing price

Decreasing contact time

Decreasing filtration run time

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Britesorb Silica Gels

BRITESORB BEER STABILIZERS	Units	HYDROGELS		HYDRATED XEROGEL	XEROGEL	
		BK75	PC5	BK200	L10	XLC
Solids content	%	36 ± 3	35 ± 3	63 ± 3	≥ 90	≥ 90
Surface area	m^2/g	680 typical	≥ 700	600 typical	550 typical	680 typical
Pore volume	ml/g	1.8	1.9	1.0	1.1	1.2
Malvern D50	µm	20 ± 3	28 ± 3	15 ± 3	15 ± 5	12 ± 5
pH target (10% suspension)	-	3	3	6	8	6
Filtration Test	seconds	≤ 200	≤ 75	≤ 650	≤ 800	≤700
Permeability	Darcy	> 0.06	> 0.18	> 0.025	>0.02	>0.1
Microbiological	cfu/g	Free from beer spoilage organisms				

- Selective adsorption with no damage to foam or flavour (controlled pore size)
- High rate of adsorption and efficiency (high internal surface area)
- Good filtration characteristics (controlled particle size distribution)

Note: PC5 and XLC are products developed for enhanced performance in Crossflow Membrane Filtration. These products are designed to minimize membrane fouling (reduced amount of fines) & maintain porosity.

Control of Silica Particle Size

Permeability of silica controlled by
- average particle size
- particle size distribution

A narrow distribution creates a more permeable silica

Small particles (fines) may result in bed packing of the filter and cause ΔP to rise sharply

Particle Size distribution of Britesorb BK75 hydrogel

Measured using a laser diffraction technique

Large particles maintain flow rate but may reduce stabilization performance (lower available area)

Control of *particle size distribution* is critical

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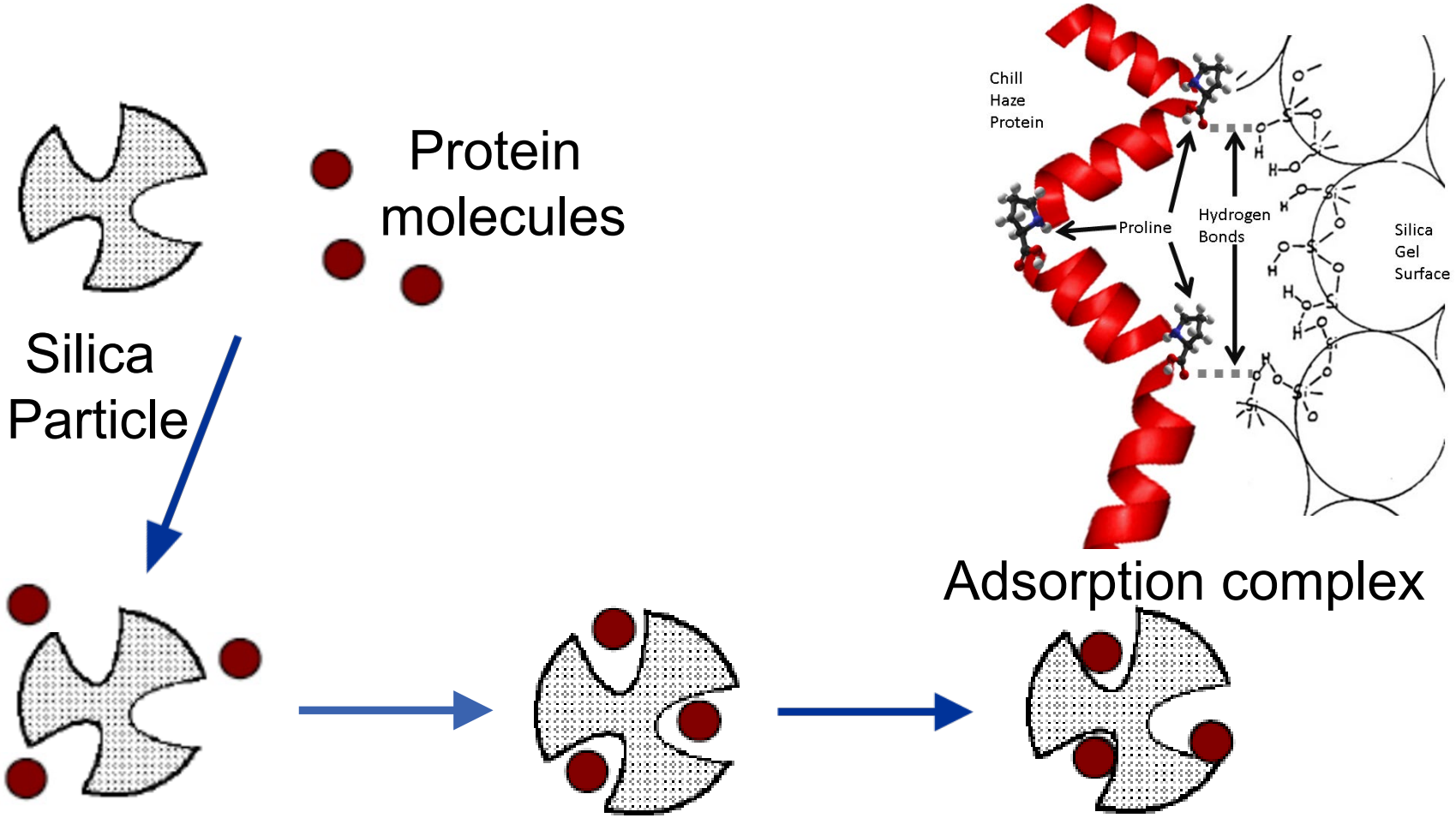
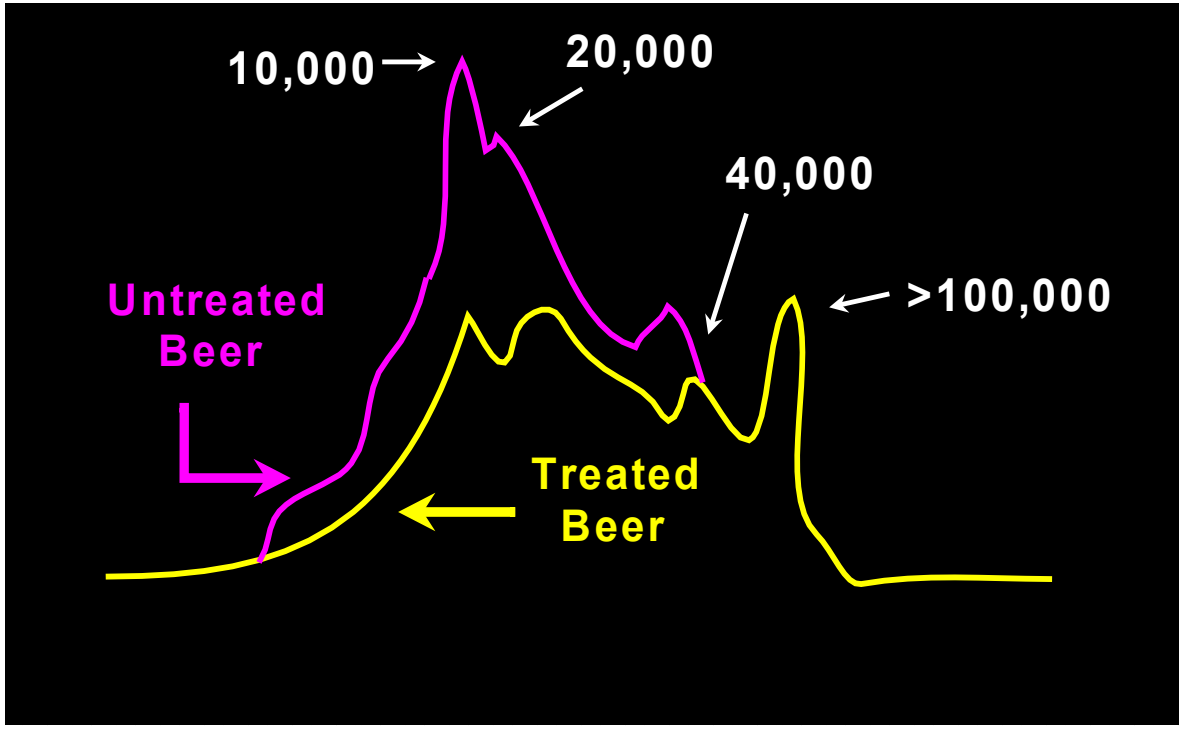
Adsorption Process

Adhesion of thin layer of molecules to the surface of a solid body



Selective Removal of Haze Active Proteins



Numbers Give Approximate Molecular Weight

Treating beer with BRITESORB® silica removes proteins of MW up to about 40 kDa but leaves untouched the higher MW proteins.

- Selective adsorption with no damage to foam or flavour (controlled pore size)
- High rate of adsorption and efficiency (high internal surface area)
- Good filtration characteristics (controlled particle size distribution)
- No contamination of beer (high purity/low metals, inert) – even accidental overtreatment causes no adverse effect
- Process Aid - no labelling requirements – silica and adsorbed protein completely removed during filtration (non-additive)
- Synthetic amorphous silica (non-silicotic) (non-crystalline)

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Practical aspects of using silica gel

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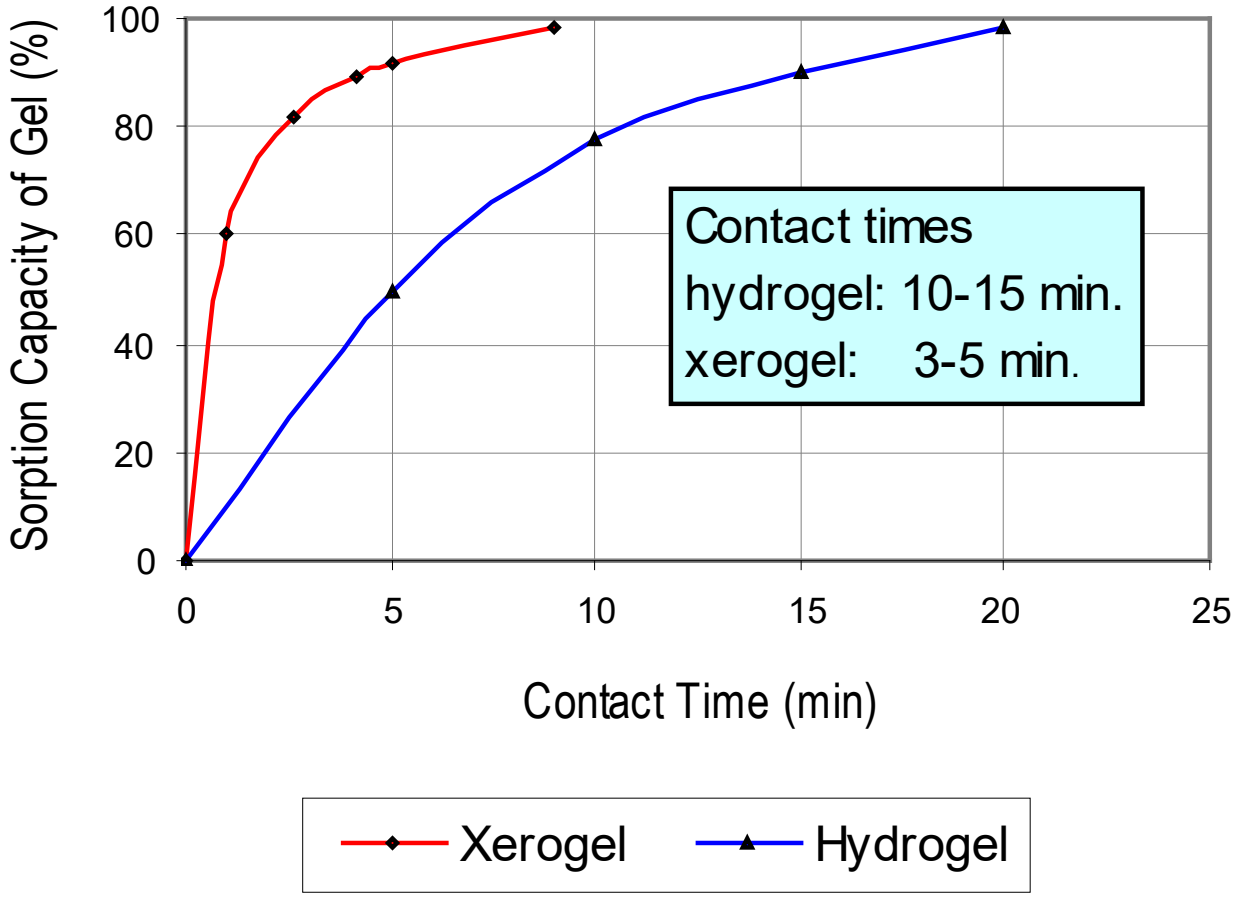
Protein Adsorption Mechanism

1. Transportation of proteins from the beer towards the silica surface (fast)

2. Adsorption on the surface (fast)

3. Diffusion of proteins into the internal pore structure (slow)
   - determines the required contact time



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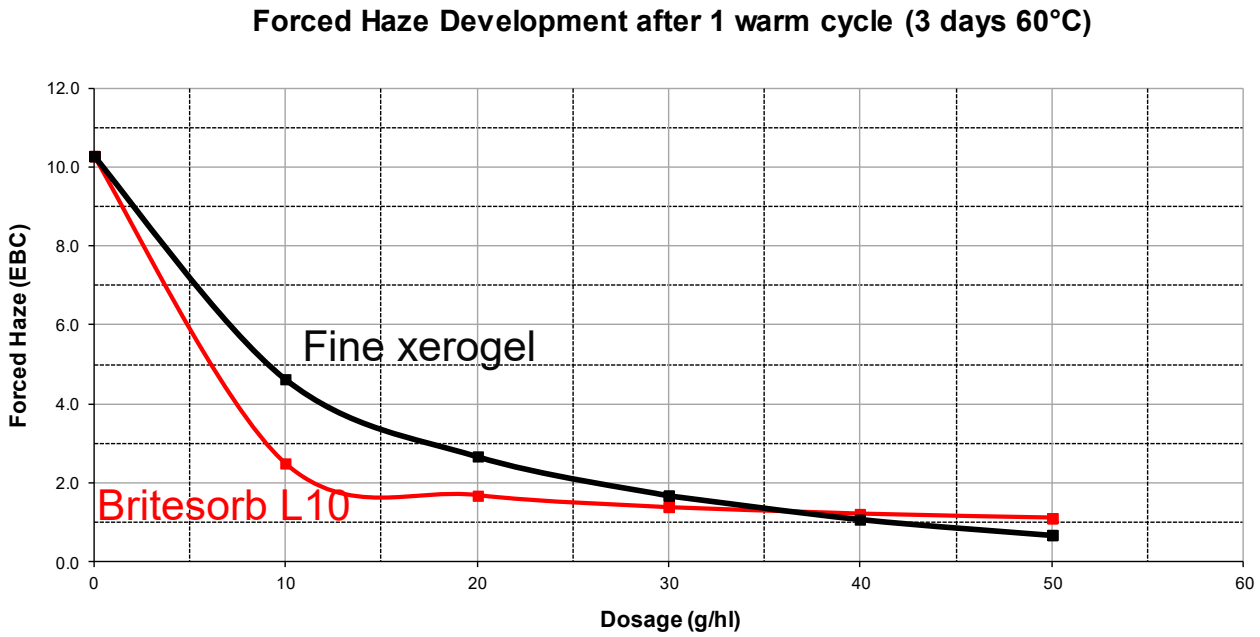
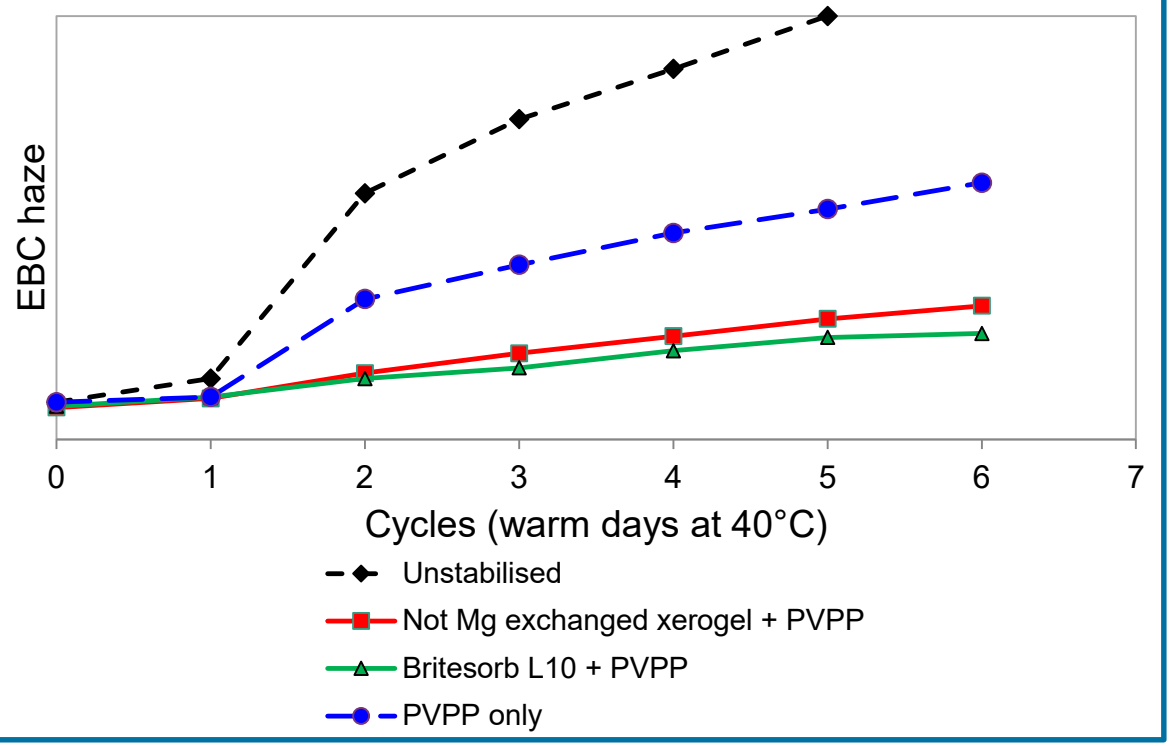
Influence of silica gel on Forced Haze formation

All malt lager



Forced Ageing:
Xerogel (50 g/hl) + PVPP (30 g/hl)



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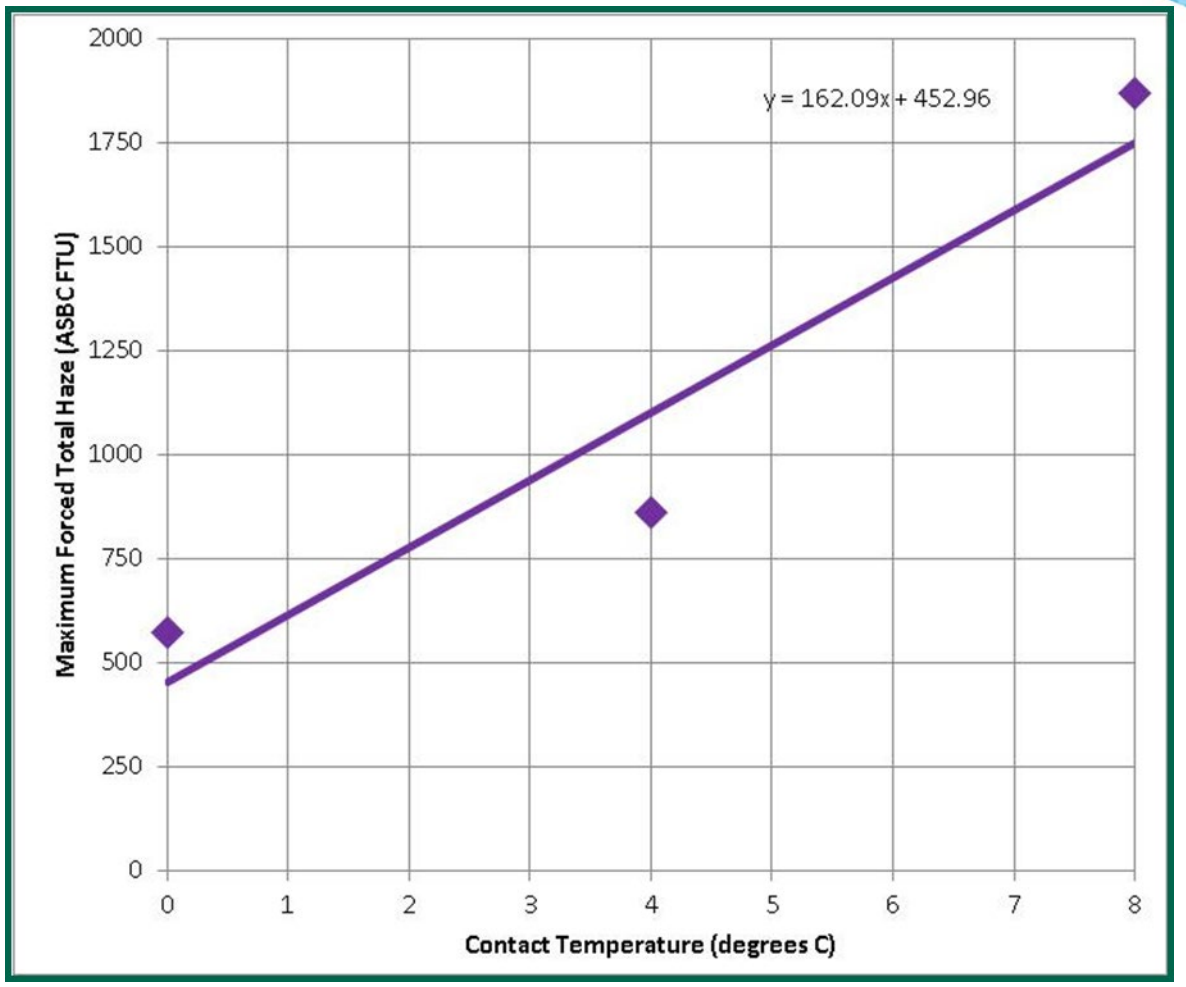
Influence of Filtration Temperature on Forced Haze formation

Increased temperature from 0°C to 8°C (32 to 46°F) triples untreated forced total haze.



Forced Total Haze of untreated beer filtered at three temperatures. Temperature during filtration affects the beer stability itself, regardless of treatment.

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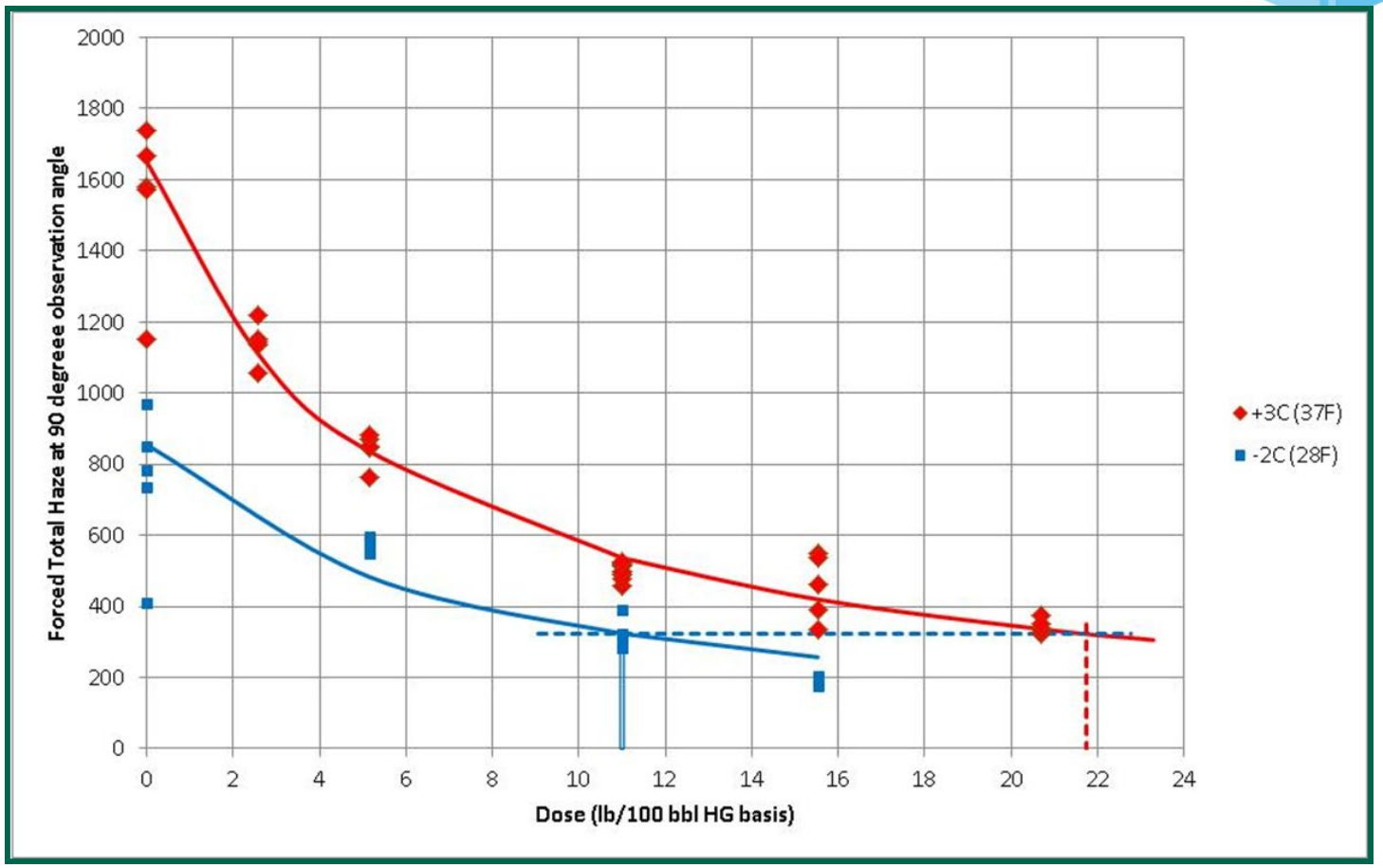
Influence of Temperature and Silica Gel dosage on Forced Haze formation

Higher silica dose corrects temperature-increased forced total haze.



Forced Total Haze of beer treated with a range of doses of BRITESORB® Xerogel at two temperatures. The dose needed at the higher temperature (red dotted line) to give the same stability (dotted blue line) as 11 lb/100 bbl at the lower temperature (double blue line) is calculated as shown.

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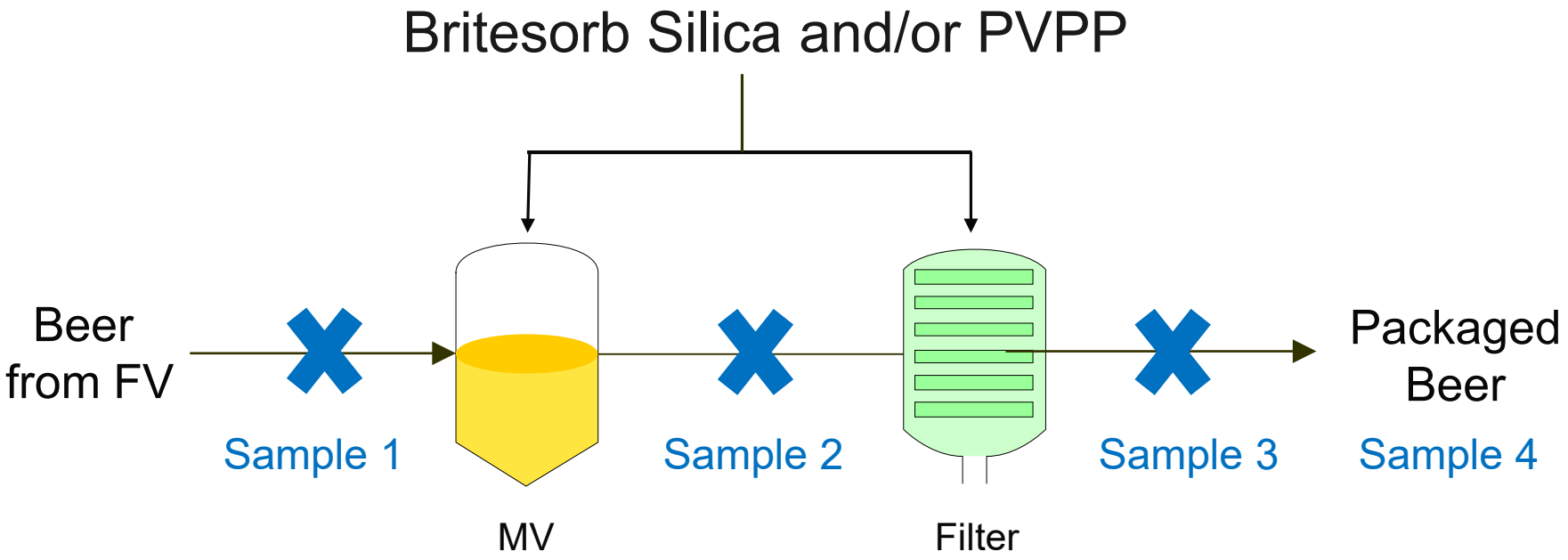
Example of Stabilization Process Audit



Sample 1 - determine initial levels of sensitive protein and tannoids
Sample 2 - determine effectiveness of treatment in storage tank
Sample 3 - determine the additional benefit of filtration treatment

Sample 4 **– laboratory analysis including forced haze results (shelf life prediction)**

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Technical Support for Customers

- **R&D in Warrington (UK)**
  - Silica product development
  - Silica related analysis
  - Microbiology lab
  - Specific beer related analysis:

    Sensitive Protein

    Tannoids

    Total Polyphenols

    Chapon Haze

    Forcing Test

    Foam stability

    Microbiology

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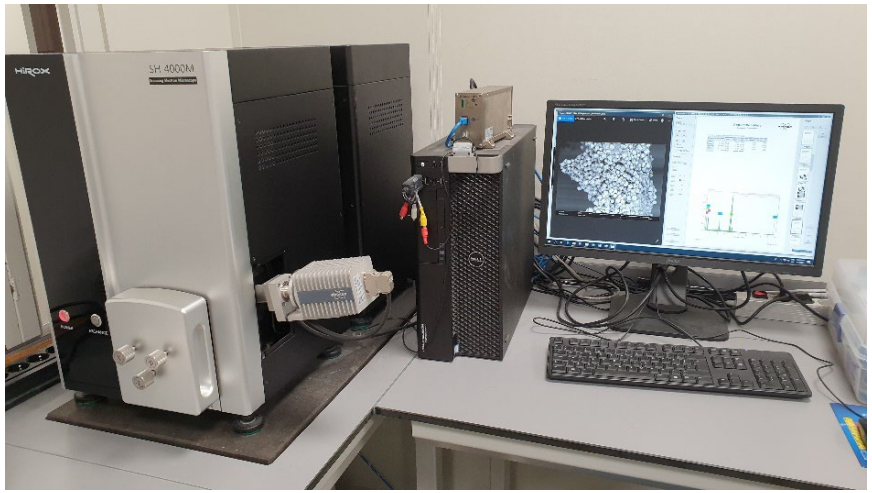
Technical Support for Customers

➢ Laboratory in Eijsden (NL)



- ➢ 3D Digital Microscope
- ➢ SEM/EDS

  Chemical microanalysis technique, which provides elemental identification

- ➢ Malvern (Particle Size Distribution)
- ➢ Gluten analysis via RIDASCREEN® Gliadin Competitive

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Britesorb: a route to ZERO waste in the brewing process

From the land…

Beer process

Option 1:

BRITESORB®

Option 2:

BRITESORB®

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… back to the land

No more Chemical Fertilzer!

ZERO WASTE

ZERO WASTE

Gluten Free Beer

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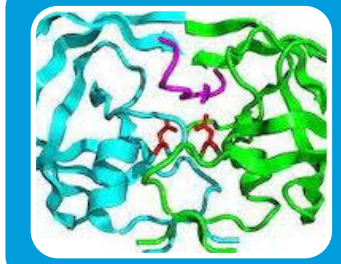
How to make gluten free beer

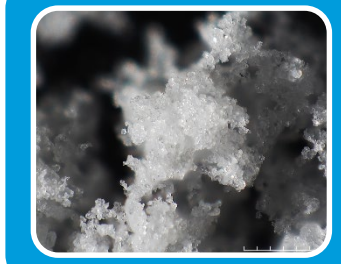
There are currently **3 main routes to produce a gluten free beer** (<20 ppm gluten content, according to the EU classification)

Gluten Free Beer

1. Use cereals or pseudo cereals that do not contain gluten, for example:
   - Quinoa
   - Maize
   - Sorghum



2. Hydrolyze the gluten by using an enzyme that hydrolyses proline-rich proteins.



3. Using a protein precipitant like tannic acid or the traditional beer stabilizer silica gel.

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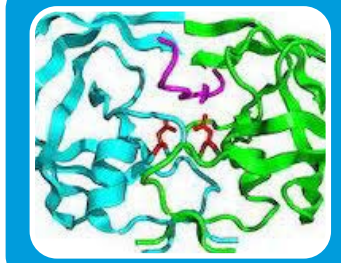
How to make gluten free beer

1. Use a malt from cereals or pseudo cereals that do not contain gluten, for example:
   - Quinoa
   - Maize
   - Sorghum

- The only route that allows gluten free labeling in the US.
- It results in beers with different aromas and flavours, when compared to malt-based beers
- It is the safest for people with celiac disease (specially for highly sensitive), as the beer does not contain any gluten.

How to make gluten free beer



2. Hydrolyze the gluten by using an enzyme that hydrolyses proline-rich proteins.

- This can be done using an <u>enzyme that hydrolyses proline-rich proteins</u>.
  - A common example is the use of the genetically modified derived enzyme Brewers Clarex®
    - Brewers Clarex® is produced from a self-cloning genetically modified GEP 44 gene carrier gep A of *Aspergillus Niger* G306
- The enzyme hydrolysation approach has the disadvantage of not removing gluten, but simply degrading it into smaller peptides
- A further limitation with the enzyme route, is that the enzyme remains in the final beer and is partially active, even when the beer is pasteurized

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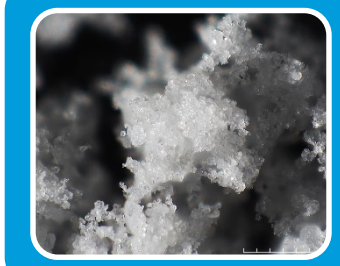
Brewers Clarex® is a trademark of DSM Food Specialties

How to make gluten free beer



3. Using a protein precipitant like **tannic acid** or the traditional beer stabilizer silica gel.

- Tannic acid is a hydrolysable tannin extracted from gall nuts. It forms insoluble complexes with proteins/polypeptides that can be removed by filtration or sedimentation
- Tannic acid is less effective in reducing gluten when compared to silica gel:
  - Needs high dosages to reduce gluten content => negative effect on the sensory quality (colour, foam and flavour) of the final beer
  - Similarly to Brewers Clarex®, tannic acid is also present in final beer

https://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FMeetings%252FCX-711-48%252FWD%252Ffa48_15e.pdf

Belleau, G.; Dadic, M.: Determination of Tannic Acid in Beer by High Performance Liquid Chromatography, Journal of the American Society of Brewing Chemists (1979), 37:4, pp. 175-179.

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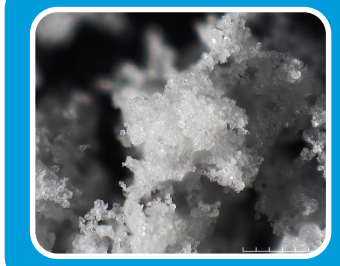
How to make gluten free beer



3. Using a protein precipitant like tannic acid or the traditional beer stabilizer **silica gel**.

- Silica gel is an amorphous, naturally derived silicon dioxide that contains a network of pores
- Highly selective adsorbent for beer haze-forming proteins, with no adverse effect on flavor, foam, color, or aroma
  - The surface chemistry includes silanol groups (Si-OH) that specifically adsorb prolamins in beer. This makes silica gel highly selective for haze protein, which contains high levels of prolamins
- Silica gel can also be added during fermentation, allowing a high reduction in gluten, without changing significantly the yeast nutritional value of beer*

*Benítez EI, Acquisgrana MR, Peruchena NM, Sosa GL, Lozano JE (2016) Effects of silica gel on reduction in gluten during several beer brewing stages. I J Food Sci Technol 51(4):920–928

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Organic Beer

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Organic beer

- Standard beer stabilizers (silica gel, PVPP,…) can be used to produce organic beers.
- Article 9 of Regulation (EC) No 834/200716 on organic production and labelling of organic products **prohibits the use of products produced from GMOs and produced by GMOs**, and this includes food enzymes produced from or by genetically modified microorganisms (e.g. Brewers Clarex®).
- Gene-editing comes under GMO rules so products with residues of enzymes derived from or produced with the help of gene-edited microorganisms/organisms have the same labelling restriction. They cannot be labelled as organic.

LABELING ORGANIC MALT BEVERAGES

	"Organic"	"Made with Organic ***"	Other
Overseen by certifier/ACA?	Yes	Yes	No*
USDA organic seal or foreign equivalent allowed?	Yes	No	No
Organic claims allowed in addition to ingredient statement?	Yes	Yes	No
Added sulfites allowed?	No	No	Yes
Non-organic hops allowed?	No	Yes	Yes
All agricultural ingredients required to be certified organic?	Yes, unless specifically allowed per National List	No, but product must be at least 70% organic	No
Ingredients produced using prohibited methods (e.g., genetic engineering) allowed?	No	No	Yes

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Crossflow membrane filtration

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Types of Filtration

Traditional

Dead end

With kieselguhr

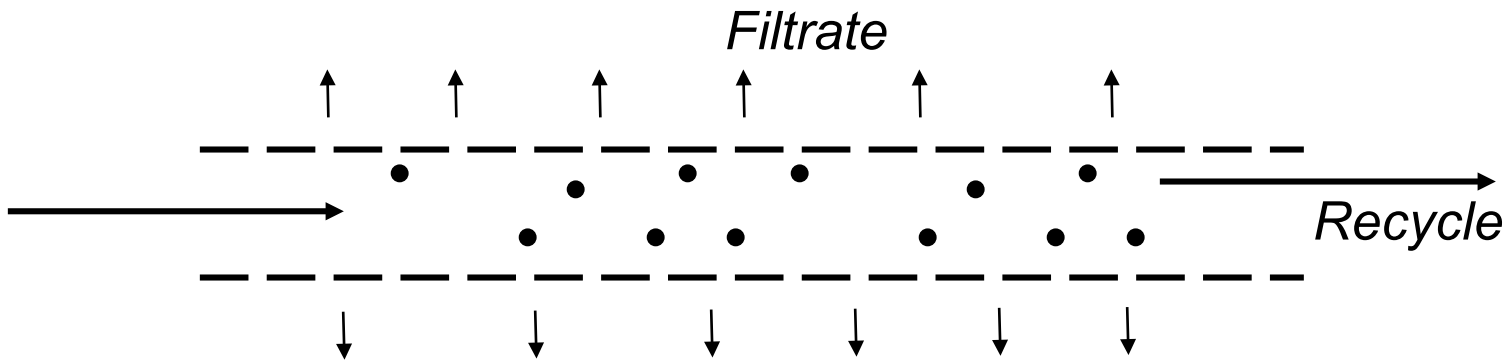
- candle filters
- leaf filters
- plate & frame filters

Crossflow Membrane

Continuous flow: In membrane crossflow filtration the crossflow suppresses the formation of a filter cake on filter media.

Without Kieselguhr

- CMF - no centrifuge (Pentair)
- CMF – with centrifuge (Pall)



0.45 µm membrane

negative pressure draws filtrate

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CMF

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BRITESORB BEER STABILIZERS

- High rate of adsorption and efficiency (high internal surface area)
- Good filtration characteristics (controlled particle size distribution)
  - Particle size distribution controlled silicas can help maintain porosity at the filter and also prevent fouling due to low amount of fines present.

PQ produces enhanced performance silica gel products for Crossflow Membrane Filtration. It is also the only supplier to offer a xerogel product for this specific application.

Summary

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Summary

- The most frequent cause of non-biological/colloidal haze is through protein-polyphenol interaction.
- PQ's Britesorb silicas assure beer shelf-life by selective adsorption of haze forming proteins.
- Britesorb Xerogel products are produced via patented process with Mg exchange, which provides higher chillproofing capability.
- Silica gel can be used to reduce the gluten content in beer.
- Silica gel is used to stabilize Organic beers.
- Both Hydrogel and Xerogel products available for CMF.
- PQ is the World's leading producer of silica gels for beer stabilization.

Philippe Cario
Brewing Commercial Manager
EMEA

Philippe.Cario@pqcorp.com
Mob. +33 7 72343315

Miguel Monsanto
Product Development Manager

Miguel.Monsanto@pqcorp.com
Mob. +31 629341181

PQ Corporation

PQ Corporation – Customer Services
CustomerService@PQCorp.com
PQ Corporation – Brewing Technical Services
Brewing@pqcorp.com