Cold Stability, CMCs and other crystallization inhibitors.

Dr Eric Wilkes
Group Manager Commercial Services
“The deposit is harmless, but the customers reaction might not be”…….potassium hydrogen tartrate…….

Bryce Rankine, 1989
Cold stability, what is it?

- **Cold stability** is essentially a wine's ability to resist the precipitation of tartrates.

- Components in wine (crystallization inhibitors) help prevent the tartrate from precipitating.
- As the wine matures or undergoes winemaking processes the levels of these inhibition compounds can change, allowing tartrate to precipitate.
- This can happen even after traditional cold stabilization.
Wine cold stabilisation methods

- Elimination/reduction of precursor compounds (e.g. potassium, bitartrate):
  - Traditional slow cold stabilization
  - Rapid contact stabilization
    - Batch
    - Continuous
  - Ion-exchange
  - Membrane processes
    - Electrodialysis

- Crystallisation inhibitors:
  - Metatartaric acid
  - Yeast mannoproteins
  - Carboxymethylcellulose (CMC)
How do they work

- They block potassium bitartrate crystal nucleation and growth by binding with one of the crystal faces preventing further growth and the appearance of visible crystals.
Why use crystallization inhibitors?

- Less impact on wine pH/TA than traditional stabilization by tartrate elimination.
- Labour and time savings.
- Lower energy impacts than traditional refrigeration.
Metatartaric acid

- First used in Europe in 1950s.
- Polymeric structure produced by heating of tartaric acid to 160 °C.

- Very effective at preventing tartrate precipitation (as long as it is there).
- Some forms may prevent Calcium tartrate.

- Stability is highly temperature dependent.
  - ~ 2 years at 10 °C
  - ~ 1 week at 30 °C

- Fining and filtration agents, particularly bentonite, can partially remove it.
- In wines treated with lysozyme, it may lead to protein-haze, even if bentonite fining is applied.
Yeast mannoproteins

- Derived from wine - a specific fraction is extracted from yeast cell walls by enzymatic hydrolysis

<table>
<thead>
<tr>
<th>Yeast Cell Wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mannoprotein</td>
</tr>
<tr>
<td>β-Glucan</td>
</tr>
<tr>
<td>β-Glucan + Chitin</td>
</tr>
<tr>
<td>Membrane</td>
</tr>
</tbody>
</table>

- Much more stable than metatartaric acid to warm temperatures.
- Effective at reventing precipitation in many wines.
- Important to perform bench trials first, as close to as bottling as possible.
- Need to add after fining and pre-filtration as fining and filtration using diatomaceous earth, perlite or cellulose fibres may remove them.
- May not be entirely suitable if a wine is supersaturated, if a high addition rate is needed (product may floculate).
- Ineffective against calcium tartrate precipitation.
- *May interact with other wine components over time and become ineffective.*
What is it?

- Polymer synthesized by the alkali-catalyzed reaction of cellulose.
What differences are there?

Substitution rates
- Number of -OH groups substituted by carboxymethyl groups.
- OIV specification is 0.6 to 0.95.

Polymer length
- Impacts solubility and viscosity.
- OIV between 17 and 300 kiloDaltons.
CMC’s don’t instantly integrate with the wine! They can take 2 to 7 days to fully integrate (depending on temperature and CMC).

Most trials have suggested that if allowed to fully integrate there is very little impact on filterability.

Important to leave this time before cellar (and tasting) operations.

A bigger issue may be actually getting them to dissolve in the first place. Some real advantages to using liquids!
Colour impacts

Cellulose and its derivatives react with tannins (including pigmented tannins) and can precipitate out colour. As such CMC’s are not recommended for reds.

Colour drop out not always apparent immediately, often only occurring after time at low temperature.

Even without significant colour dropout can get hazes.

Can be used with some rose but need to do trials first.
Haze formation

Protein can crosslink with CMC’s to form hazes. This can happen post filtration and be temperature linked. Wines to be treated with CMC must be protein stable.

Some literature has raised issues with certain metal ions also leading to cross linking and hazes. Only an issue for di and tri-valent species (eg, copper and iron) but no confirmed reports of this in wine.
Wine style and age

Trials to date have given positive results for all wine styles tested. Some question with younger wines with very high $T_{-sat}$. Also some evidence that in very young wines other compounds may be interacting with CMC’s removing them from the equation.

### Cold Instability Level

<table>
<thead>
<tr>
<th>CMC Treatment</th>
<th>Cold Instability Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unstre...</td>
<td>3</td>
</tr>
<tr>
<td>CMC 1_L</td>
<td>2</td>
</tr>
<tr>
<td>CMC 1_H</td>
<td>1</td>
</tr>
<tr>
<td>CMC 2_L</td>
<td>1</td>
</tr>
<tr>
<td>CMC 2_H</td>
<td>1</td>
</tr>
<tr>
<td>CMC 3_L</td>
<td>0</td>
</tr>
<tr>
<td>CMC 3_H</td>
<td>0</td>
</tr>
<tr>
<td>CMC 4_L</td>
<td>0</td>
</tr>
<tr>
<td>CMC 4_H</td>
<td>0</td>
</tr>
</tbody>
</table>

For **Colombard wine**:

- $T_{sat} = 19.6 \, ^{\circ}C$
Variety impact on CMC effectiveness

<table>
<thead>
<tr>
<th>Cold Instability Level</th>
<th>Variety 1</th>
<th>Variety 2</th>
<th>Variety 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Low</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>
Effects of CMC on white wine colour and turbidity

![Graph showing the effects of CMC on white wine colour and turbidity. The x-axis represents different doses of CMC (Untreated, Low, Medium, High), and the y-axis represents the ratio to the untreated sample. The graph includes bars for OD 280 nm (blue), OD 420 nm (green), and Turbidity (red).]
What else?

Calcium stability

- Trials published to date suggest that CMC’s don’t appear to be particularly effective in the prevention of calcium tartrate instability.
- This may because of the different crystal structure of CaT.

Flavour impacts

- There are reports that CMC’s can impact wine mouth feel.
- Highly wine and CMC dependent.
- Make sure trials give time for full integration.

Testing

- Saturation temp gives no indication of CMC induced stability but does give an indication of suitability.
- Brine test does work.
- Mini contact can be impacted depending on seeding rates.
CMC summary

1. They can work!
2. Best used when packaging ready (cellar bright and protein stable).
3. Need 2 to 7 days post treatment before filtration.
4. Wines should have a Sat-Temp in the region of <20.
5. Some wine styles may have other components that could reduce the effectiveness of a given dose of CMC.
6. Not a great idea for reds that you want to keep colour stable and haze free.
7. Must choose a CMC that is workable for your cellar operations.
8. Need to adjust testing regimes.
Questions?