Heat stabilisation: past and present

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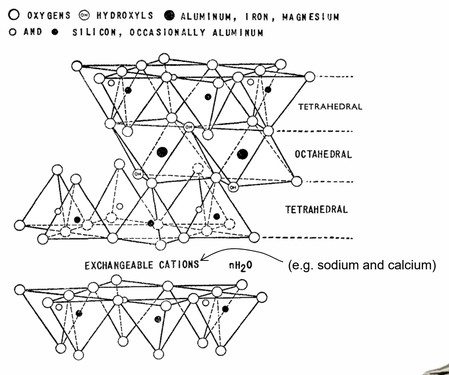
AWRI



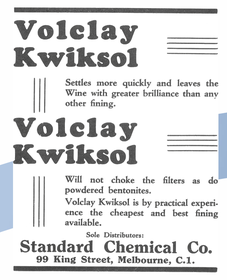
Montmorillonite

This is the key mineral constituent of bentonite that provides swelling and protein adsorption properties.


(2) Le kaolin (argile très pure, matière première de la fabrication des porcelaines), qui est un silicate d'alumine hydraté, a déjà été préconisé pour l'élimination des matières albuminoïdes précipitables et la stabilisation des vins blancs (Sur les matières albuminoïdes des vins blancs, J. Ribéreau-Gayon. *Annales des Falsifications*, 1932).

Bentonite not the first clay for wine

Spanish clay from Lebrija has long been used for fining sherry wines, and was subsequently used in many other countries. Kaolin was trialled in France for protein removal shortly before bentonite was discovered in the USA. Spanish clay and kaolin were much less effective protein removers than bentonite. Use of clays for fining wines has also been mentioned in much earlier texts such as *Geoponika*, the 10th century Byzantine Greek farming manual.



American Colloid Co., Trade Literature Collection, Smithsonian Libraries

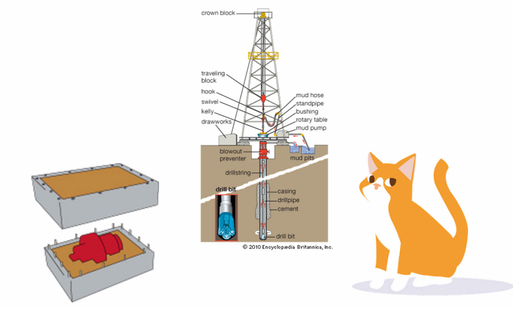
Consistent dry particle size

Bentonite can be hard to prepare and can clump. American Colloid Company found that if they limited the dry particles to a larger tight size range that it would dissolve much more easily. This was KWK bentonite. It is not entirely clear but it appears that this bentonite was probably not granulated from finer powder, rather just a crushed bentonite sieved to select a particular size fraction.

Bentonite

German calcium bentonite

In 1948, German-mined Geisenheimer Erde calcium bentonite with a low calcium solubility began to be sold and became popular in Germany.

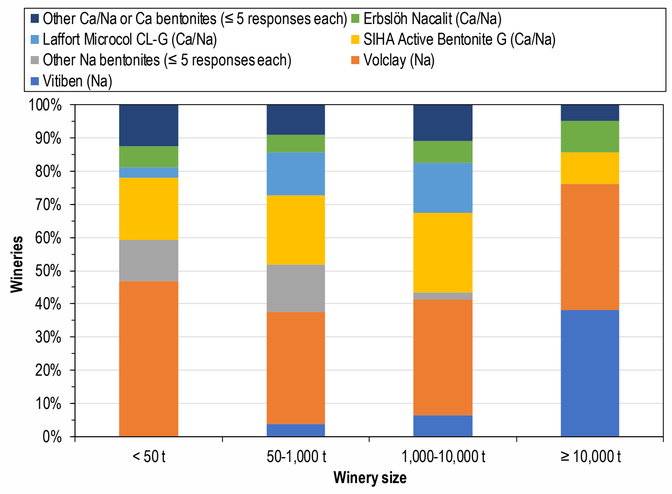


Bentonite - *"the clay of 1,000 uses"*

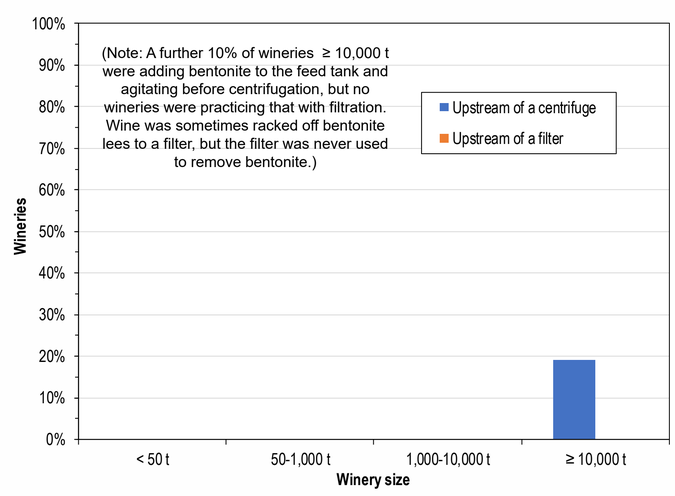
The wine industry is a relatively small user of bentonite. Its swelling and adsorptive properties mean that it is used in many industries, including as foundry sand cast binder, in drilling fluids and for cat litter.

Bentonite for fining wine

In 1934 in the USA, Saywell recommended the use of bentonite for wine clarification. It was a major milestone, as prior to that there was no efficient way of heat-stabilising wine (kaolin would need 10 times the dose, stabilisation by heat treatment was sometimes imperfect). Saywell's initial article established that bentonite both clarified and stabilised wine to heat, but did not clearly establish that it removed protein (Jean and Pascal Ribéreau-Gayon point this out in their articles and books, while acknowledging the importance of bentonite). By 1940, bentonite had largely supplanted all other methods for wine clarification in California. Adoption of bentonite in France was slower.



Most common bentonite used



Using in-line dosing

Sodium-calcium granulated blends

In 1969 the Erblsöh wine division (a division created based on the popularity of Geisenheimer Erde) released NaCalit. This was a blend of sodium and calcium bentonites that sought to achieve the greater protein binding of sodium bentonites with the lower lees volumes of calcium bentonites. This product was also granulated from finer powder, making it even easier to prepare without clumping.

Australian winery practices in 2016 (www.awri.com.au/survey)

Lees compaction during removal or juice/wine recovery without downgrade

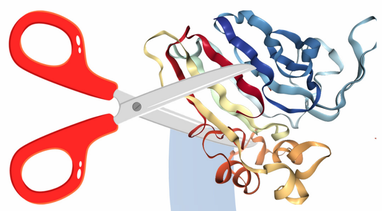
One of the biggest issues with bentonite is the large lees volumes it causes and that juice/wine is typically recovered by rotary drum vacuum filtration, during which it is oxidised and diluted with water. Use of centrifuges for bentonite separation and cross-flow filtration for lees reprocessing partly counteract this.

Erhöhung der Eiweißstabilität im Wein.

Walter J Ä G E R

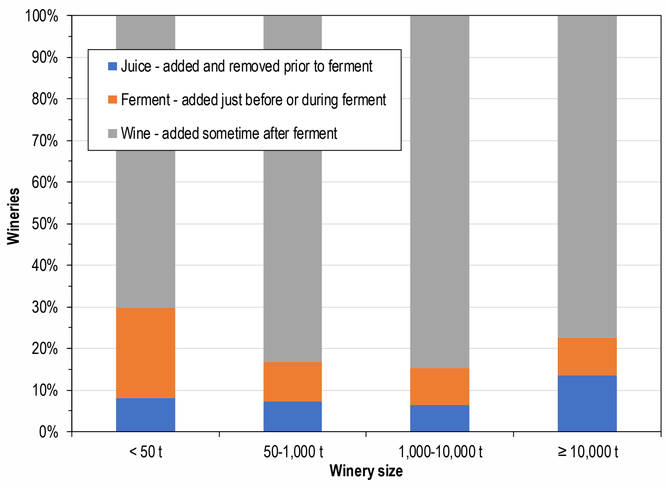
30.6.53

"Wenn zu einem ausreichenden enzymatischen Eiweißabbau der Wein auch auf 35 bis 40°C erwärmt werden muß,"



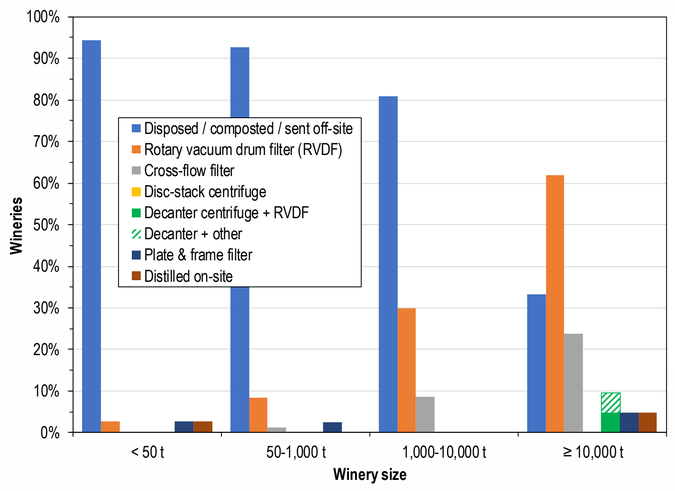
Proteases

Proteases that break up proteins responsible for haze were first investigated in the 1950s, but found to require the use of elevated temperatures. This has so far not met acceptance from wine producers because of concerns about possible sensory impacts and the heating infrastructure requirements.

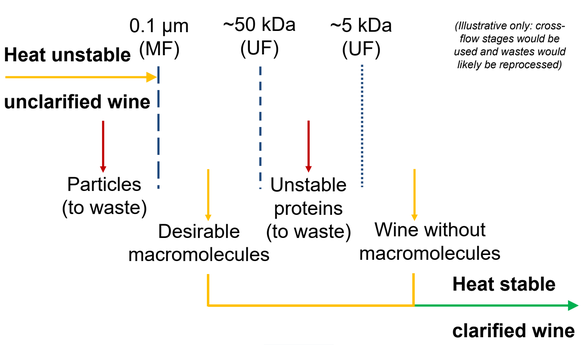


Most common timing of largest addition

(Note: Many wineries added bentonite to wine, but it was prior to the first separation from yeast lees. For example, in ≥ 10,000 t wineries, while only 10% were adding their largest bentonite dose during ferment, 60% were removing bentonite in combination with their yeast lees)



Method of bentonite lees processing



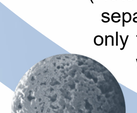
Multi-stage ultrafiltration – an opportunity?

Cross-flow ultrafiltration is a process that would not need additives/processing aids and that could be integrated as additional stages in automated cross-flow microfiltration equipment. The multiple stages may alleviate the issues of macromolecule stripping experienced with single-stage ultrafiltration in the 1980s. Key R&D question: can commercial membrane materials be found with suitably low adsorption and pore sizes that would consistently sandwich the proteins?

Alternative adsorbents

Many alternative adsorbents have been trialled, but none adopted. Reasons include:

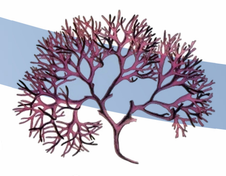
- High price (bentonite is cheap)
- High dose requirements
- Small particle size (higher doses and price could be partly counteracted by using them in regenerable packed beds, but small particles can create other issues like high pressures/low flow rates)
- Risks of causing hazes with minor over-fining
- Preparation difficulties
- Sensory impacts (Some bentonites can remove flavour/aroma and there are debates about whether this is practically significant or not – it is plausible that some alternative adsorbents removing proteins by similar mechanisms could have the same issues)



Chromatography and industrial grade resins

Zirconia

A white metal oxide most well known for its use in the production of synthetic gemstones (cubic zirconia).

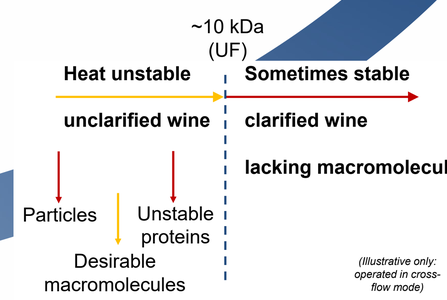


Carrageenan

Polysaccharide from red algae commonly used as a thickener and stabiliser of dairy products, and also as a beer fining agent (sometimes in impure forms – e.g. Irish moss).

The alternatives

Single-stage ultrafiltration



Ultrafiltration was trialled in the 1980s at laboratory scale and as part of early industrial-scale investigations of cross-flow filtration as a means of clarifying juice or wine and simultaneously removing proteins. Nominally ~10 kDa membranes were not effective, retaining larger molecular weight polysaccharides important to wine quality and experiencing some bleed-through of proteins. Negative experiences with single-stage cross-flow ultrafiltration likely contributed to early wine industry negativity towards cross-flow filtration.

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