# Heat stabilisation: past and present

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Effective WATER STOPPAGE

100%

90%

80%

70%

60%

50%

40%

30%

20%

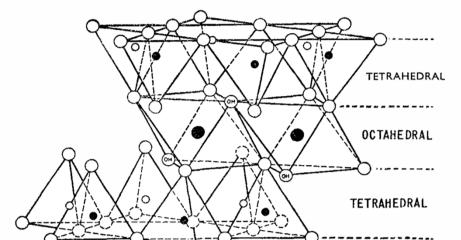
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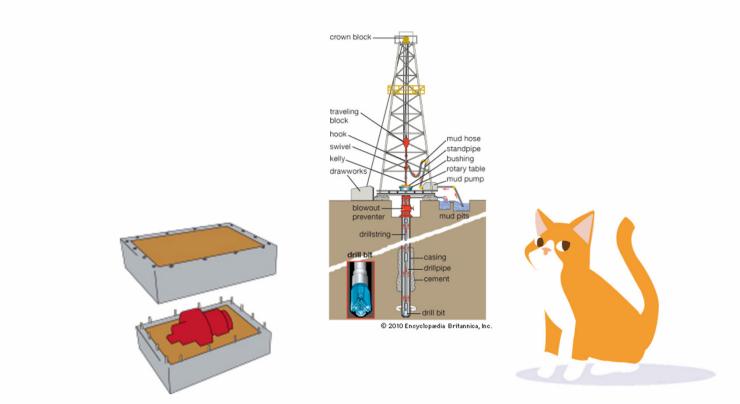
*Corresponding author's email: simon.nordestgaard@awri.com.au* 

🔿 OXYGENS 🐵 HYDROXYLS 🌑 ALUMINUM, IRON, MAGNESIUM O AND . SILICON, OCCASIONALLY ALUMINUM

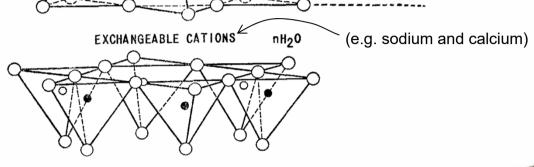


(2) Le kaolin (argile très pure, matière première de la fabrication des porcelaines), qui est un silicate d'alumine hydraté, a déjà été préconisé pour l'élimination des matières albuminoïdes précipitables et la stabilisation des vins blancs (Sur les matières albuminoïdes des vins blancs, J. Ribéreau-Gayon.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









#### Montmorillonite

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

#### Clarification of Wine

University of California Darkalan Ca

RIAL AND ENGINEERING CHEMISTR

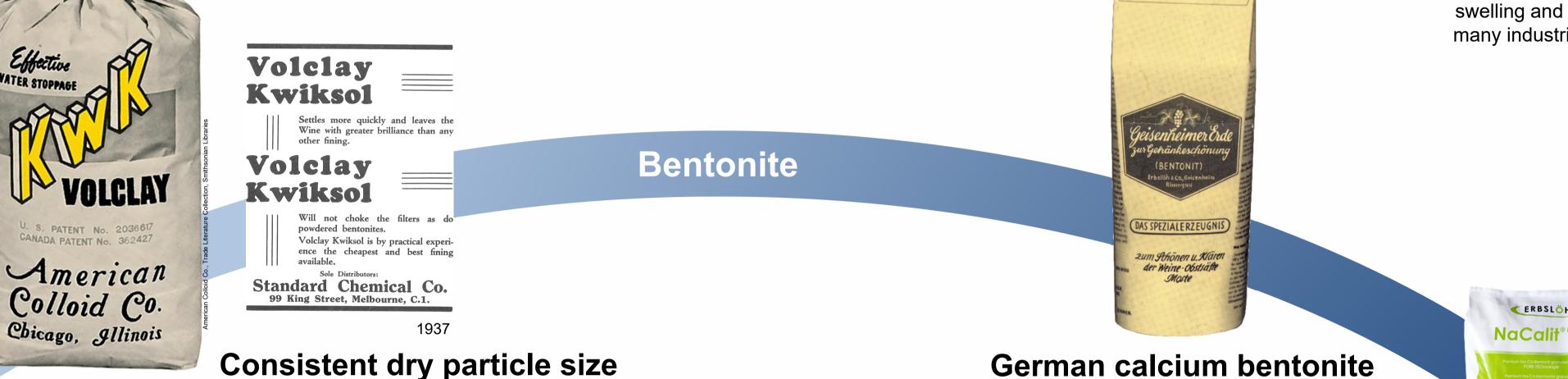
L. G. SAYWELL, University	of California, Berkeley, Calif.	
The clouding of wine is a problem important to the wine industries of Europe, Australia, and the United States. In general, the causative factors may be similar, but the composition of the wines from the different production areas may vary considerably and thus change the nature of occurrence of clouding. In relation to Cali-	use increases the rate of flow and the brilliancy of the filtrate, but results with different wines vary widely. In general, 0.1 or 0.2 per cent of filter aid has been found most satisfac- tory. An important criticism of the use of filter aids has been that the iron content of the wine was increased thereby. This condition apparently depends upon the filter aid used.	
fornia wines, many European wines are high in tannin and acidity, while certain Australian wines are markedly low in tannin. As a result, wine types that may be stable in France may develop a cloud in California or Australia. Further, newer wines are often cloudy and some type of clarification then becomes a routine part of the manufacturing process.	A certain diatomaccous earth of grayish color had been used in a plant with very unsatisfactory results, added iron being sus- pected as a possible factor. Analysis of the untreated wine in- dicated an iron content of 17.3 parts per million, while the treated wine contained 51.5 p. p. m. Evidently, where the only differ- ence in treatment had been the use of the earth, the earth had increased the iron content.	
Because many of the methods of clarification formerly used for California wires are now being found inadequate, it has become necessary to study the general process of wine clarification with the object of securing a permanently bril- liant product. Previous California practice (2) utilized gelatin, egg white,	With a better quality of diatomaceous earth, repeated experi- ments indicate a relatively small or even negligible increase of iron content. Two samples were filtered, using 60 per cent of a 60-50 mixture of Super-CeI and Hi-Fio. The original untreated samples contained 14.5 and 17.5 p. m. of iron, while the sam- ples treated with filter aid contained 12.5 and 16.4 p. p. mori-	
isinglass, and tannin as the chief clarification or fining agents. Inadequate or improper use of these materials generally re- sults in a reclouding of the clarified product, and often tank quantities of wine from juice of the same pressing and same later treatment will vary in their stability to cloudingMany	nally 18.7 p. p. m. of iron were treated with 0.1 per cent Super- Cel and with 0.1 per cent of a 60-90 nixture of Super-Cel and Hi- Flo. These portions were found to contain a final iron content of 18.2 and 17.6 p. p. m. of iron, respectively?. All iron analyses reported in this paper are by the method of Stugart (9). Treatment with gelatin, egg white, isinglass, or tannin,	
factors may be responsible for this occurrence. The iron content of such clouded wines is often higher than that of the unclouded wines, and consequently, the presence of the larger amount of iron has been held to cause the clouding. This may be confirmed by adding iron to a clear sample and thereby inducing clouding, a control remaining clear.	with or without a diatomaceous earth filter aid, may result in only a temporary clarification followed by reclouding, and occasionally may not even effect an initial clarification. This situation is comparable to that occurring with wine vinegar, where experiments covering three years' time (6) have shown	
Thereby inducing crowding, a control remaining treat. For clearing with gelatin a high grade of product is used, about one part of gelatin being added to 9000 or 10,000 parts of wine. (Rapid approximation of quantities may be secured by taking the weight of one gallon of wine to be 8.3 pounds, 130 ounces, or 3.7 kg.) The gelatin is dissolved in warm water, mixed with a few gallons of the wine to be treated, and added with thorough	that a consideration of the colloidal properties of the liquid considerably aided in adapting methods for clearing. On this basis the use of the natural hydrous silicate of alumina, bentonite, was tried and found very satisfactory in compari- son to other methods.	
few gallons of the wine to be treated, and added with thorough stirring to the larger volume being clarified. For clearing with egg white, the material (free of volk) is mixed of the start of the start of the white from a tegg, and the whites from 4 to 8 eggs are required for each 100 gallons of wine. This original aqueous solution of egg white should be duited with	Use or BENYONITE It is desirable to remove any excess of iron at the time of clarification. The earlier methods of clarification and iron removal involved the use of gelatin and tannin with adration $(\delta)$ , an oxygen treatment alone $(\delta)$ , or the use of potassium	
about 10 volumes of wine before adding to the tank quantity. Mixing should be thorough. The amount of isinglass required may vary considerably, one part of isinglass in 7000 to 25,000 parts of wine being used. The optimum concentration about db determined on smaller quanti-	ferrocyanide to precipitate the iron (?). A general discussion of the relation of iron to clouding or cases is given by Rib- ereau-Gayon and Peynaud (?) for French wines. None of these methods involved the use of bentonite, but the results with vincegr: suggested the desirability of testing its use with	
thes of wine at the time of application. The estimated quantity of singlass is placed in a small volume of cold water for several hours, or until much of the swelling to generate. The mixture is thoroughly stirred, heated more over any gassed through a seve (or heavy cloth), put colded. So if quartities of wine are then added, with one start at stirring, ut a 1 is full consistency is obtained. The start for clarify $z$ with so, nev by both the several volume of the several volum	wine. Preliminary ats indicated that clarification by bentonite to a satisfact on as judged by repeated chilling and heating that for explain to sunlight and by standing at 30° C. cualitative for for indicated a reduction in corput.	DECT
added one to two is added to 5000 c mended in order tend to produ the official m (Castman 1)	The second of the second of the second secon	OMING
U. S. P	role of iron in causing cloudiness pendent upon its state of oxidation $(3,2)$ the formic iron baing associated with the	
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#### **Bentonite for fining wine**

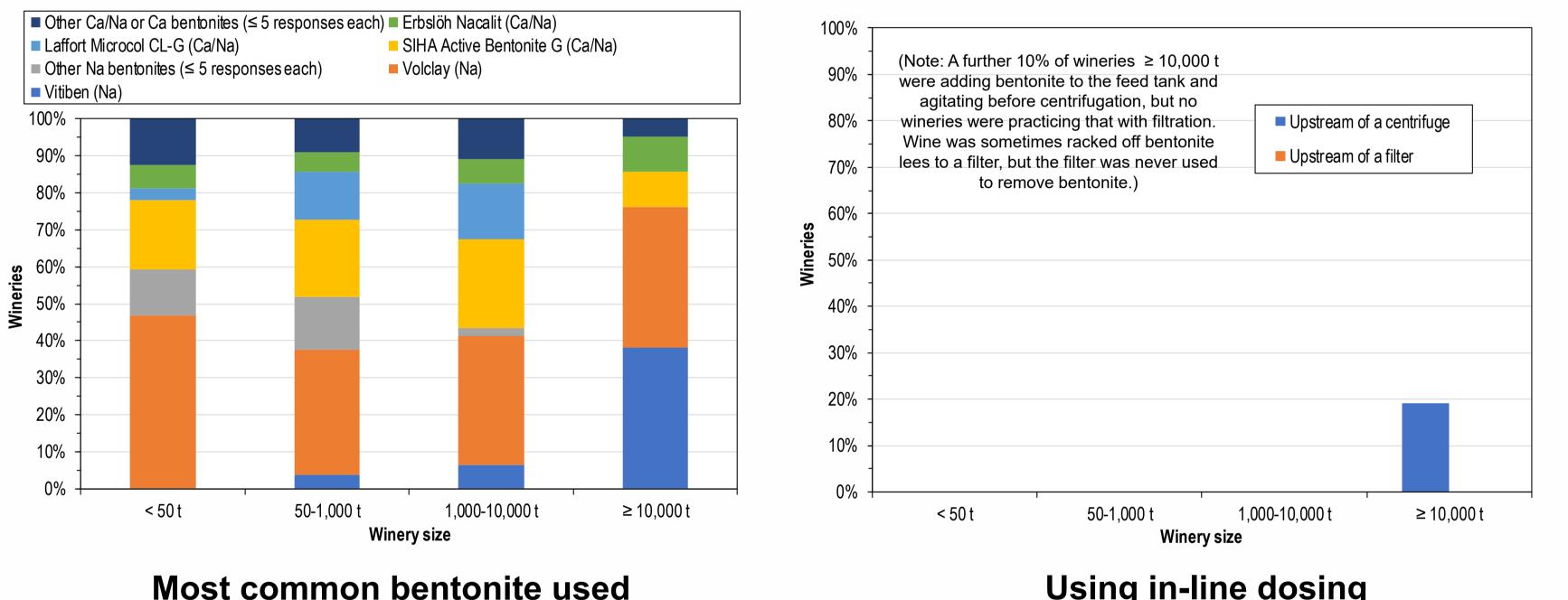
In 1934 in the USA, Saywell recommended the use of bentonite for wine clarification. It was a major milestone, as prior to that there was no efficient way of heatstabilising wine (kaolin would need 10 times the dose, stabilisation by heat treatment was sometimes imperfect). Saywell's initial article 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.

#### 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 10<sup>th</sup> century Byzantine Greek farming manual.



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 - "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.

**ERBSLÖH** 

### 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.



Using in-line dosing

In 1948, German-mined Geisenheimer Erde

calcium bentonite with a low calcium solubility

began to be sold and became popular in

Germany.

## Lees compaction during removal or juice/wine recovery without downgrade

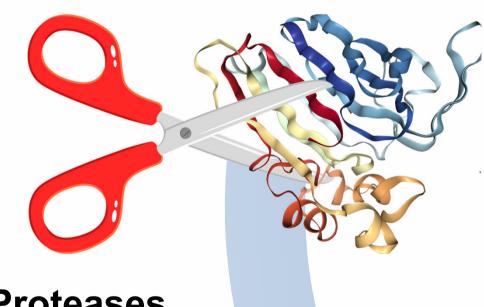
One of the biggest issues with bentonite is the large lees volumes it causes and that juice/wine is typically recovered by rotary drum vacuum filtration, during which it is oxidised and diluted with water. Use of centrifuges for bentonite separation and cross-flow filtration for lees reprocessing partly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

#### Erhöhung der Eiweißstabilität im Wein.

Walter JÄGER

#### 30.6.53

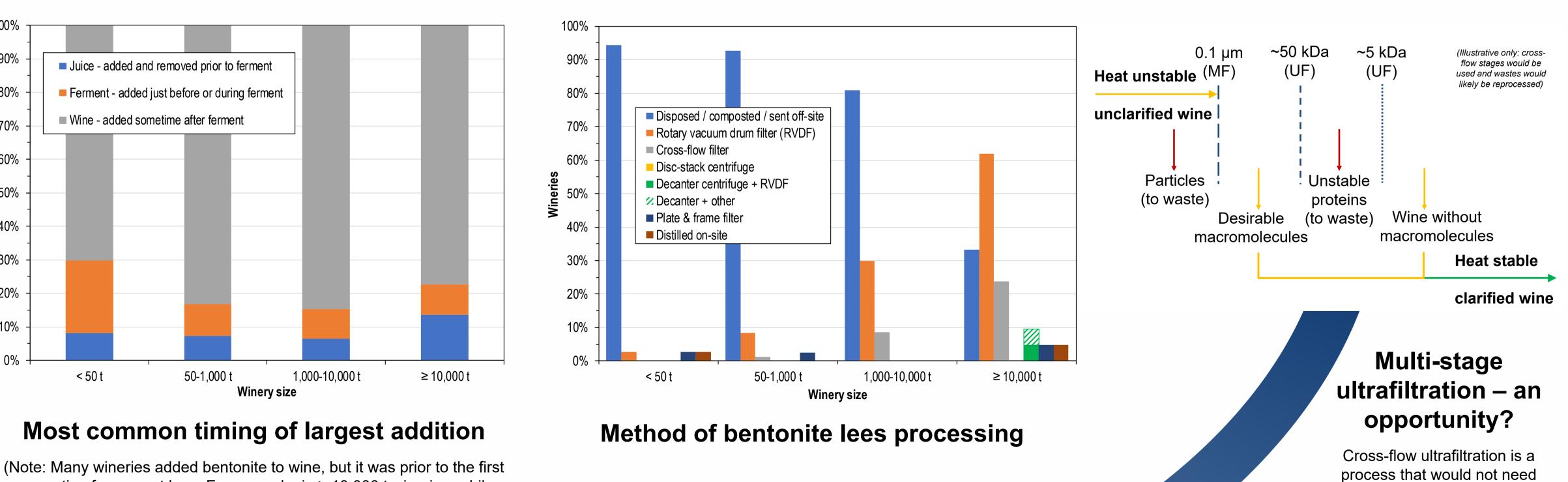
Wenn zu einem ausreichenden enzymatischen Eiweißabbau der Wein 66 auf 35 bis 40°C erwärmt werden muß, auch



#### **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.

## Australian winery practices in 2016 (<u>www.awri.com.au/survey</u>)



#### **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)

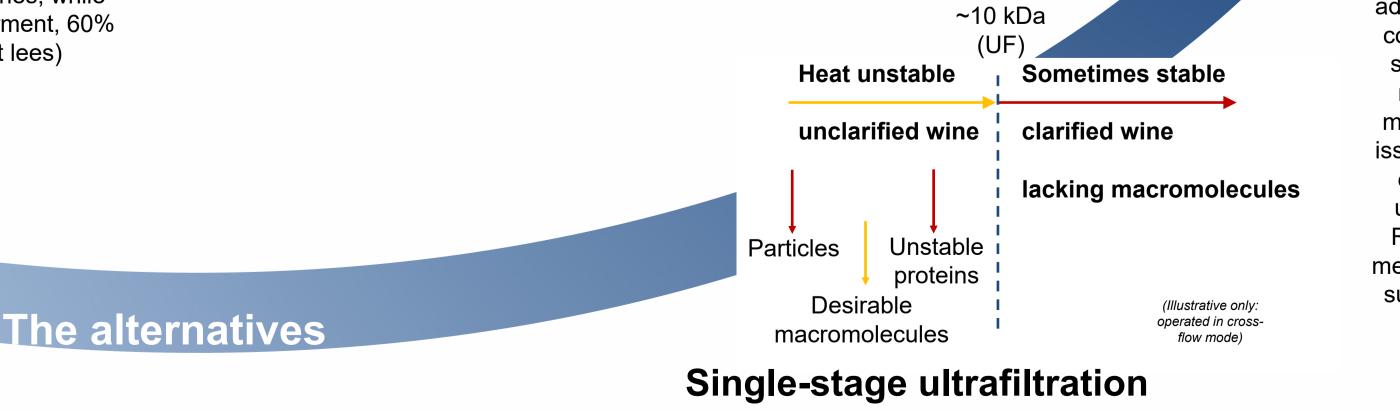
separation from yeast lees. For example, in  $\geq$  10,000 t wineries, while only 10% were adding their largest bentonite dose during ferment, 60% were removing bentonite in combination with their yeast lees) Chromatography and industrial grade resins Zirconia

A white metal oxide most well known

for its use in the production of synthetic gemstones (cubic zirconia).

> 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).

Carrageenan



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?

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.

The Australian Wine Research Institute

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