An evaluation of some commercial bentonites in terms of performance, characteristics and cost effectiveness

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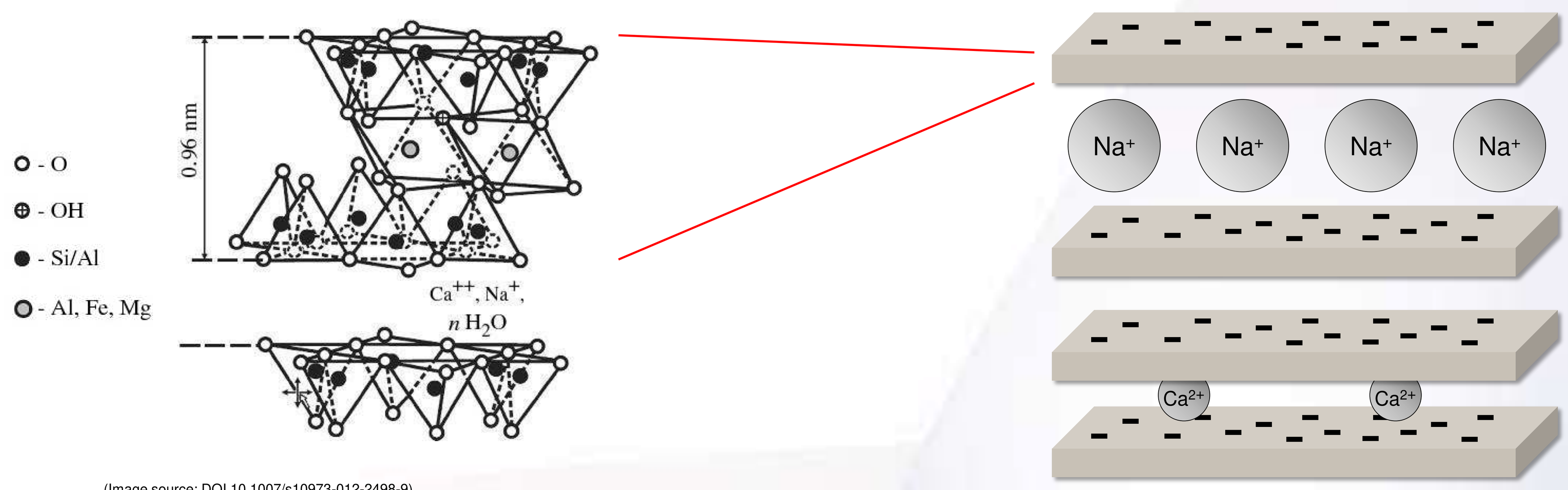
Introduction

In order to remove heat unstable proteins from wine, the addition of bentonite, a clay, composed of aluminium silicates (Rankine & Emerson, 1963) is rehydrated in water and added to juice or wine. Heat unstable proteins are almost exclusively derived from grapes, however the presence of non-grape derived proteins may influence the total wine stability through their interaction with non-protein stability factors (Batista et al, 2009). Protein haze forms in finished wine when heat unstable proteins denature as a result of temperature fluctuations. A number of factors can influence the formation of protein hazes with each wine being unique in terms of its protein stability, consequently bentonite fining trials are required for all wines to determine the addition rates required in order to remove all heat unstable proteins (Hsu & Heatherbell, 1987). Adsorption of the wine proteins onto the bentonite sheets occurs as a result of charge differentials and the proteins are removed. This method of protein stabilisation is almost universally practiced in winemaking, resulting in bentonite being the most commonly used fining agent in white wine production.

Bentonite is a natural product with many different forms. The primary difference between bentonites is the makeup of the exchangeable metal ions (cations) in the interlayer spaces between the aluminium silicate sheets. Oenological bentonite (mainly composed of montmorillonite) is generally classified as Na or Ca bentonite, referring to the dominant cationic species within the bentonite interlaminar regions. These bentonites exhibit different physical behaviours in wine and there are advantages and disadvantages to each. The prevailing form of bentonite used in the Australian wine industry is Na, with mixed, exchanged and Ca bentonites not as widely used. This usage pattern is not mirrored in Europe, where Ca bentonite usage is far more prevalent.



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Types of bentonite and their characteristics

The dominant exchangeable cation within bentonite exerts considerable influence on its efficacy as an oenological fining agent. Sodium bentonites are characterised by their higher swelling in water due to the lower charge density of the Na^+ cation, which exposes a large number of surfaces for adsorption, resulting in lower addition rates being required (Rankine & Emerson, 1963). However, this results in poor compaction during the settling process and relatively large quantities of wine remaining within the bentonite lees. Bentonites containing the divalent Ca^{2+} cation exhibit considerably different physical properties. The greater charge density of Ca^{2+} (double that of Na^+) results in a substantially lower swelling capacity compared with sodium bentonite (Alther, 2004), hence more rapid rehydration. However, this exposes fewer charged surfaces to the wine, thus higher addition rates are required. Importantly, the reduced swelling results in greater lees compaction and, as a result, wine recovery is significantly increased (Rankine & Emerson, 1963). Activated bentonites are calcium bentonites that have had some Ca^{2+} ions replaced with Na^+ ions via treatment with sodium carbonate. These products exhibit increased adsorption efficiency relative to calcium bentonites, yet their compaction is improved relative to sodium bentonites (Gougen et al., 2003). Time required for lees settling is also an important consideration for winemakers when selecting bentonite for protein stabilisation, particularly in high throughput winemaking operations where tank space is limited and rapid protein stabilisation is required. Comparative studies of these properties are limited, however research has indicated that calcium bentonites form lees faster than sodium bentonites due to their lower swelling capacity and the greater charge density of the divalent Ca^{2+} cation (Leske et al., 1995; Bowyer & Moine-Ledoux, 2007).

Lees compaction

One critical but often overlooked bentonite characteristic that strongly impacts cost effectiveness is lees compaction. Large volumes of wine are lost through bentonite lees, and although there are techniques to recover some of this wine they usually lead to quality loss through oxidation. Eight commercially available bentonites were evaluated using a multi-varietal 2012 white wine: 3 sodium-dominant bentonites, 2 calcium-dominant bentonites, SIHA Puranit, SIHA Puranit UF and SIHA Active bentonite G. Bentonite solutions were prepared as 5 % w/v suspensions, which were stirred for 15 minutes before being left to swell at room temperature for 24 hours. Prior to bentonite additions, stock suspensions were mixed for a further 15 minutes. Additions were made at the determined levels to achieve protein stability by the heat test, the samples mixed and monitored over 5 days. SIHA Active bentonite G, with a lees volume of 1.6 %, produced the lowest lees volume of all tested bentonites despite having the highest required addition rate of 2.0 g/L. The next lowest lees volume was over twice that of SIHA Active bentonite G.

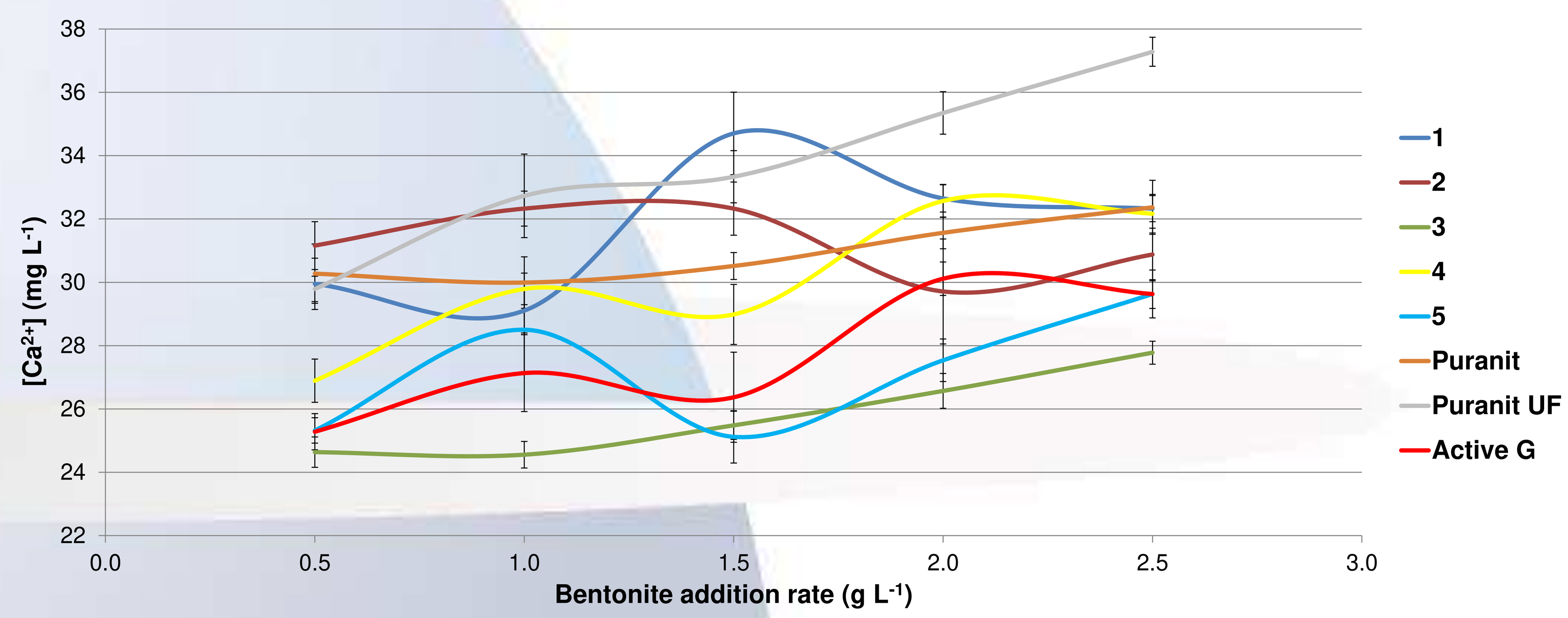
Bentonite	Dominant exchange cation	Addition rate for protein stabilisation (g/L)	Final lees volume (%)
Bentonite 1	Na	0.6	4.0
Bentonite 2	Na	0.7	3.8
Bentonite 3	Na	0.7	6.5
Bentonite 4	Ca (some Na exchange)	1.5	5.2
Bentonite 5	Ca	1.1	4.0
SIHA Puranit	Ca	1.8	3.4
SIHA Puranit UF	Ca	1.8	5.1
SIHA Active G	Ca (some Na exchange)	2.0	1.6

Metal ion transfer into wine from bentonite use

Protein removal in wine is an ion-exchange process, hence cations present within the bentonite are transferred into the wine during fining. Of the dominant exchangeable cations within bentonite, it is calcium that causes the most trepidation amongst winemakers due to the potential formation of calcium tartrate. Calcium tartrate has the lowest solubility of all mineral salts commonly found in wine (Abgueguen & Boulton, 1993) and, due to complex interactions with other compounds within the wine matrix, its solubility is difficult to predict (McKinnon et al., 1995). Winemakers generally avoid introducing calcium into wine wherever possible in order to minimise the instability risk, hence some winemakers are reluctant to use calcium bentonites as protein stabilisation agents, despite the significant processing advantages that they can offer.

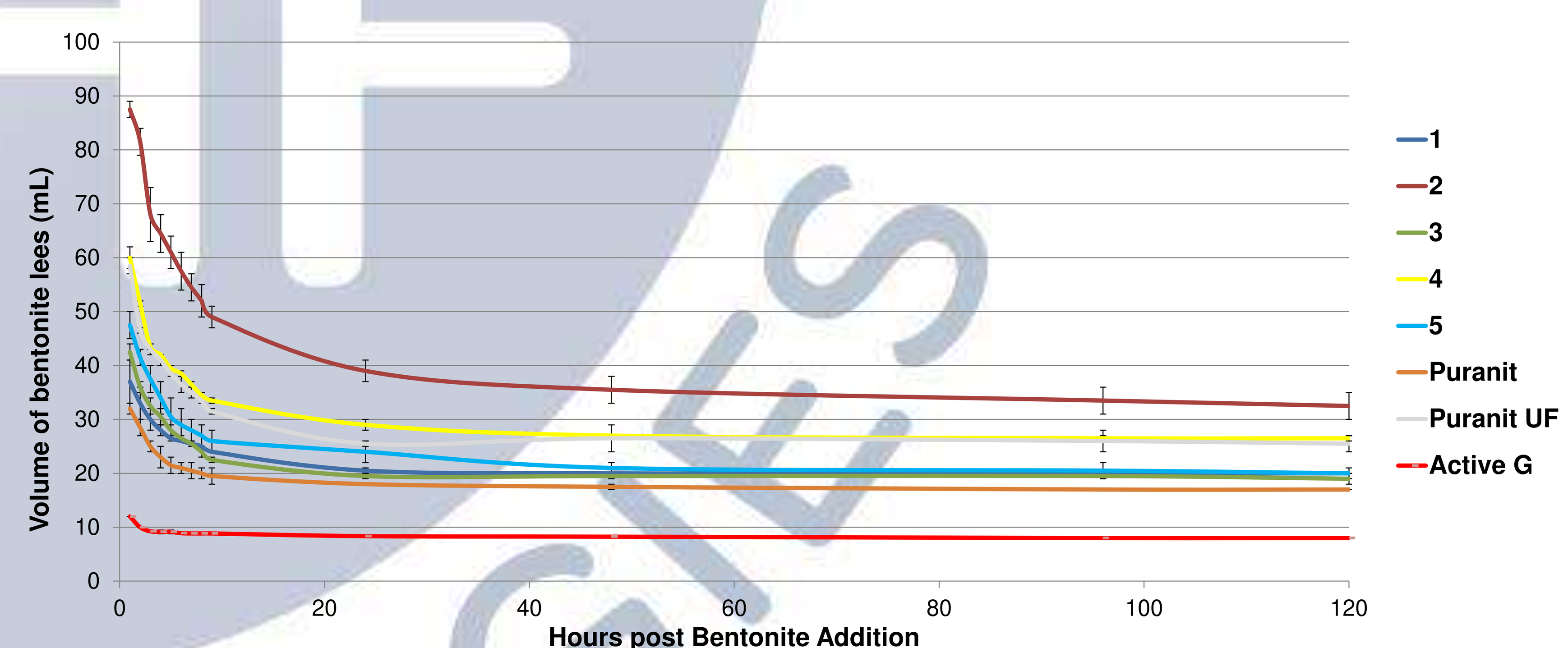
The magnitude of this risk has not been quantified in Australian wine and represents a gap in the scientific literature, hence measurements were made to determine the transfer of calcium into wine during bentonite treatments. The data are presented below.

Bentonite	Addition Rate (g/L)	$[Ca^{2+}]$ (mg/L)	$[Ca^{2+}]$ Increase (mg/L)
Control wine	0	27.0^{d}	0.0
Bentonite 1	0.6	29.8^{c}	2.8
Bentonite 2	0.7	30.8^{bc}	3.8
Bentonite 3	0.7	25.2^{e}	-1.9
Bentonite 4	1.5	29.0^{c}	2.0
Bentonite 5	1.1	27.9^{d}	0.9
SIHA Puranit	1.8	31.6^{b}	4.6
SIHA Puranit UF	1.8	36.0^{a}	8.9
SIHA Active G	2	30.1^{bc}	3.1



Swelling time, kinetics of lees compaction and ease of use

Besides ion exchange capacity and lees volume, other factors are important during application in a winery, such as ease of use, time required for preparation (rehydration) and the speed at which the bentonite forms its lees. As a general trend, sodium bentonites were slower to settle than the calcium bentonites. In the case of SIHA Active G settling was so rapid that, once rehydrated, the stock supernatant can be discarded to minimise water additions to levels far below that of sodium bentonites, and to avoid adding bentonite fines that can take longer to settle (see stock solution in photo, lower left).



Cost-benefit analysis

To determine the cost effectiveness of a bentonite treatment there are many factors to consider, principally purchase price, addition rates and % wine loss. Using the measured lees percentages and valuing wine at $5 /L (e.g. bulk wine price) and $20 /L (e.g. bottled wine price), the amount of money lost by a winemaker in lees during a bentonite treatment is shown to be significant. Bentonite purchase price and addition rate become insignificant when compared with wine loss through lees.

Bentonite	Approximate bentonite cost for required stabilisation rate ($ for 10 kL treatment)	Lees % after 5 days	Lees volume (L) per 10 kL	Value of wine lost in lees per 10 kL valued at $5/L	Value of wine lost in lees per 10 kL valued at $20/L
Bentonite 1	$ 10	4.0	400	$ 2000	$ 8,000
Bentonite 2	$ 15	3.8	380	$ 1900	$ 7,600
Bentonite 3	$ 15	6.5	650	$ 3250	$ 13,000
Bentonite 4	$ 30	5.2	520	$ 2600	$ 10,400
Bentonite 5	$ 30	4.0	400	$ 2000	$ 8,000
SIHA Puranit	$ 45	3.4	340	$ 1700	$ 6,800
SIHA Puranit UF	$ 45	5.1	510	$ 2550	$ 10,200
SIHA Active G	$ 45	1.6	160	$ 800	$ 3,200

Conclusion

Calcium bentonites require higher addition rates and cost more than sodium bentonites, yet their greater ease of use, speed of preparation, faster settling and superior lees compaction can make them the better choice on both practical and economic grounds. In this study the best-performing bentonite in terms of lees compaction, speed of settling, cost-effectiveness and minimising water additions was SIHA Active G, and an addition of 2.0 g/L increased $[Ca^{2+}]$ by only 3.1ppm.

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