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 and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009). Protein haze forms in finished wine when heat unstable proteins denature and are almost exclusively derived from grapes, however the presence of non-grape factors (Batista et al., 2009).

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. Commercial bentonite (mainly composed of montmorillonite) is generally classified as Na or Ca bentonite, referring to the dominant cationic species within the bentonite interlamellar 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.

Types of bentonite and their characteristics

The dominant exchangeable cation within bentonite exerts considerable influence on its efficacy as an adsorption medium. 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 Ca2+ cation exhibit considerably different physical properties. The greater charge density of Ca2+ (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 some Ca2+ ions replaced with Na+ ions via treatment with sodium carbonate. These products exhibit similar physical properties to calcium bentonites, yet their compaction is improved. 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 Ca2+ cation (Leskie et al., 1995; Bowyer & More-Bledsoe, 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. Bentonites containing the divalent Ca2+ cation exhibit considerably different physical properties. The greater charge density of Ca2+ (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 some Ca2+ ions replaced with Na+ ions via treatment with sodium carbonate. These products exhibit similar physical properties to calcium bentonites, yet their compaction is improved. 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 Ca2+ cation (Leskie et al., 1995; Bowyer & More-Bledsoe, 2007).

Bentonite Addition Rate (g/L) [Ca2+] (mg/L) [Ca2+] Increase (mg/L)

Control wine 0 27.4 0.0
Bentonite 1 0.5 29.8 0.0
Bentonite 2 0.7 30.8 0.0
Bentonite 3 0.7 105.0 0.0
Bentonite 4 1.5 29.0 0.0
Bentonite 5 1.1 27.6 0.0
SIBA Puranit UP 1.6 34.5 4.0
SIBA Puranit 1.8 36.9 0.0
SIBA Active G 2.0 36.1 0.1

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 filtering. Of the dominant exchangeable cations within bentonite, it is calcium that causes the most trepidation amongst winemakers due to the potential formation of calcium tartarate. Calcium tartarate has the lowest solubility of all mineral salts commonly found in wine (Abgüeguén & Boulton, 1990) 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.

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 SIBA Active G settling was so rapid that, once rehydrated, the stock supernatant could 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).

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, SIBA Puranit UP and SIBA Active G. Bentonite solutions were prepared as 5% w/v suspensions, which were stirred for 15 minutes before being left to stand 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 stabilisation. The efficiency relative to calcium bentonites, yet their compaction is improved. Comparative studies of these properties are limited; however research has indicated that calcium bentonites form lees faster than sodium bentonites, yet their lower swelling capacity and the greater charge density of the divalent Ca2+ cation (Leskie et al., 1995; Bowyer & More-Bledsoe, 2007).

Bentonite 5
Bentonite 4
Bentonite 3
Bentonite 2
Bentonite 1
SIBA Purent
SIBA Puranit UP
SIBA Active G

SIBA Puranit UP 1.6 34.5 4.0
SIBA Puranit 1.8 36.9 0.0
SIBA Active G 2.0 36.1 0.1

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.

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 minimizing water additions was SIBA Active G, and an addition of 2.0 g/L increased [Ca2+] by only 3 ppm.