
Changes in metal concentrations in wines treated with different bentonites

Introduction

The presence of certain grape-derived proteins can lead to the formation of hazes in white wines – a problem often referred to as heat instability. Bentonite fining is the usual method used to remove these proteins from wine before they can cause issues. Bentonites consist of negatively charged clay particles bound to positively charged metal ions, such as sodium or calcium. At low pH (pH < 4.0) haze-forming proteins in wine are positively charged and can therefore undergo ion exchange with the metal ions on the surface of the bentonite. The strength of ion exchange is influenced by wine acidity (AWRI 2017).

The two most common types of bentonite used in winemaking are sodium bentonite and calcium bentonite. In addition to sodium and calcium ions, these bentonites contain trace metals such as copper, manganese and iron, which can also be exchanged with proteins and transferred into wine (Catarino et al. 2008). The maximum allowable concentrations of these metals are regulated in certain international markets, with the limits for five key metals in five different markets shown in Table 1 (AWRI 2016).

Table 1. The maximum concentration allowed in wine for five different metals in five different markets (AWRI 2016).

	Maximum concentration				
	Arsenic	Manganese	Iron	Copper	Lead
Argentina	0.2 mg/L	–	–	1 mg/L	0.15 mg/L
Ontario (Canada)	0.1 mg/L	–	–	1 mg/L	0.2 mg/L
China	–	2 mg/L	8 mg/L	1 mg/L	0.2 mg/L
European Union	–	–	–	1 mg/L	0.2 mg/kg
Russia	0.2 mg/kg	–	10 mg/L	5 mg/L	0.3 mg/L

Metals such as iron and copper (and to a degree manganese) can affect the shelf-life of wine by catalysing oxidation/reduction reactions and also influence the generation of volatile sulfur compounds during bottle ageing.

Comparing different bentonites

A study was set up to investigate the settling characteristics, protein removal ability and metal transfer properties of three bentonites in two different white wines at two different pH levels (pH 3.0 and 3.4). The types of bentonites used were a natural sodium bentonite (Na), an activated sodium and calcium bentonite (Ac Na-Ca), and an activated sodium bentonite (Ac Na). Activated bentonites are bentonites that have undergone treatment to

improve their protein binding abilities and ion exchange rates (Catarino 2008). The selected wines included a heat-stable white wine (from which haze-forming proteins had previously been removed) and a heat-unstable white wine (still containing haze-forming proteins) with their pH levels adjusted to 3.0 and 3.4 using tartaric acid and calcium carbonate respectively. The heat-stable wine was included as a type of control, allowing any effects caused by the presence of the proteins in the unstable wine to be assessed.

A standard bench-top fining trial was conducted to determine the appropriate bentonite dosage rates for the unstable wine at the two different pH levels. These rates were then used to treat both the unstable wines (2 L volumes) and stable wines (1 L volumes), with settling carried out over six days. The settling characteristics were assessed by measuring the volume of lees present after the settling period. The wines were also analysed for metal content using inductively coupled plasma mass spectrometry (ICP-MS).

Settling characteristics

Table 2 shows the volume of lees present after treatment, expressed as a percentage of the total wine volume, for the bentonites investigated in these experiments.

The lees percentage increased significantly for the two sodium bentonites with protein present (unstable wine) relative to the stable wine, with the effect seen at both pH 3.0 and 3.4. However, the same relationship was not seen for the sodium-calcium bentonite.

There was an obvious pH effect for the Ac Na bentonite which was not as significant in the Na bentonite. At the higher pH, the lees percentage for Ac Na was lower, suggesting that the flocculating capabilities of the bentonite were affected by pH.

Table 2. Experimental settling characteristics for bentonites under investigation in all wine samples determined after a settling period of six days.

Bentonites	Unstable wine		Stable wine	
	Dosage rate (g/L)	Lees percent (%)	Dosage rate (g/L)	Lees percent (%)
pH = 3.0				
Na	0.5	4.29%	0.5	2.14%
Ac Na-Ca	1.0	3.48%	1.0	4.75%
Ac Na	1.7	4.40%	1.7	2.90%
pH = 3.4				
Na	0.6	4.40%	0.6	2.26%
Ac Na-Ca	1.3	4.17%	1.3	3.94%
Ac Na	1.1	4.06%	1.1	2.09%

The bulk of the settling appeared to occur quickly (within a few hours) and was not significantly affected by the pH of the wines. In the unstable wine samples the activated bentonites appeared to settle slightly quicker than the sodium bentonite but the clarity of the wine was not necessarily improved. In the stable wines, the bentonites settled at approximately the same rate.

Effect of wine pH and protein stability on the metal exchange of different bentonites

Results of the metal analysis conducted on the wines are shown in Table 3. The numbers show the difference in metal concentration between the untreated control wines and the treated wine samples (average of duplicate treatments), with positive values indicating an increased metal concentration due to the bentonite treatment and negative values indicating a decreased concentration. The differences in metal concentrations between the control samples of each wine at the different pH levels is due to trace levels of metals in the tartaric acid and calcium carbonate used for the pH adjustment.

The ion exchange process increased the iron content in the stable wines by approximately 90% at pH 3.0 and 63% at pH 3.4. There was a similar increase in the unstable wines from an undetectable amount of iron in the control wines to concentrations ranging from 0.4 to 0.7 mg/L in the treated wines. No copper was detected in three of the wine samples; however, copper was observed to decrease in the more acidic unstable wine (pH 3.0). The concentration of arsenic in all the wine samples was very low when compared to the regulatory limits (Table 1). Nevertheless, the increase in the arsenic concentration (up to a maximum of 80% in the stable wine) should be noted. A similar increase was seen for manganese.

Wine pH also had a significant effect on the ion exchange, particularly for zinc, vanadium, strontium and lead. For zinc, vanadium and strontium, the extent of metal transfer was lower in wines at pH 3.0 than at pH 3.4. Conversely, the transfer of lead increased in more acidic wine, but levels remained well below the regulatory limits.

The presence of haze-forming proteins also influenced the transfer of metals into the wine. In the case of nickel, the increase in concentration was higher in the stable wine at a pH of 3.0 but there was little difference at a pH of 3.4. For calcium, the concentration in the stable wines increased whereas it decreased in the unstable wines. These results may be due to the proteins present in the unstable wine interacting with the calcium ions and removing them from the wine during fining. These results suggest that overdosing a wine with bentonite could cause a larger proportion of the metals present in the bentonite to be transferred into the wine during the fining process.

Table 3. Change in metal concentration caused by bentonite treatment, with positive values indicating an increase in metal concentration and negative values indicating a decrease in metal concentration. All concentrations are expressed in µg/L.

Samples	Arsenic (As)	Cadmium (Cd)	Calcium (Ca)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)	Iron (Fe)	Lead (Pb)	Lithium (Li)
Stable wine pH = 3.0									
Ac Na	1.10	0.00	12500	1.50	4.60	0.00	600	5.60	-0.60
Ac Na-Ca	1.00	0.00	4500	1.00	1.00	0.00	300	3.60	-0.55
Na	1.60	0.00	3000	1.00	0.45	0.00	500	7.65	0.45
Stable wine pH = 3.4									
Ac Na	0.50	0.00	13000	1.00	2.75	0.00	400	0.45	0.30
Ac Na-Ca	1.20	0.00	35500	1.00	1.40	0.00	200	2.65	0.55
Na	1.55	0.00	11000	0.50	0.35	0.00	350	1.60	1.45
Unstable wine pH = 3.0									
Ac Na	0.00	-2.70	-40000	1.00	4.60	-100	700	9.10	0.30
Ac Na-Ca	0.00	-2.70	-67000	1.00	1.30	-100	500	6.80	0.50
Na	2.50	-2.70	-52000	0.00	0.50	-100	600	9.30	1.70
Unstable wine pH = 3.4									
Ac Na	0.00	0.00	-28000	1.00	3.30	0.00	600	2.50	-0.30
Ac Na-Ca	2.00	0.00	-42000	0.00	1.80	0.00	400	1.30	0.70
Na	2.80	0.00	-46000	0.00	1.20	0.00	600	2.90	1.00

Samples	Magnesium (Mg)	Manganese (Mn)	Nickel (Ni)	Potassium (K)	Sodium (Na)	Strontium (Sr)	Vanadium (V)	Zinc (Zn)
Stable wine pH = 3.0								
Ac Na	-3500	250	6.30	-1500	-10000	23.50	1.00	-141.00
Ac Na-Ca	-4500	100	1.70	-4000	-8000	49.50	2.00	-10.00
Na	-6500	100	2.00	-500	-6000	125.50	0.00	18.00
Stable wine pH = 3.4								
Ac Na	-3000	200	3.45	-3500	-9000	40.50	1.00	-21.00
Ac Na-Ca	-1000	100	1.75	-1000	-5000	99.00	3.00	1.50
Na	-6000	0	1.20	-1500	-5000	121.00	0.00	-3.50
Unstable wine pH = 3.0								
Ac Na	-7000	200	3.70	-38000	-1000	-90.00	2.00	-54.00
Ac Na-Ca	-5000	100	-2.00	-25000	1000	-11.00	3.00	37.00
Na	-11000	100	-2.70	-34000	2000	22.00	0.00	37.00
Unstable wine pH = 3.4								
Ac Na	-2000	300	3.90	-32000	-2000	100.00	0.00	246.00
Ac Na-Ca	-2000	200	0.60	-48000	1000	157.00	3.00	279.00
Na	-4000	100	0.30	-32000	3000	205.00	0.00	290.00

Overall the stable wines experienced concentration increases higher than those seen in the unstable wines at optimum dosage rates. Further experiments to observe the effect of overdosing unstable wine samples with bentonite are recommended to see if this effect on metal concentration increase is replicated.

Summary

The focus of this study was the change in metal concentrations seen in white wines treated with different types of bentonites and the influence of wine properties on the bentonites' performance characteristics.

The metal transfer for all bentonites used was significantly affected by the pH and the presence or absence of haze-forming proteins in the wine. It is important to note the changes in the iron, copper, lead, arsenic and manganese concentrations in the wine samples because of the regulations imposed by certain markets on levels of these metals and their impact on wine shelf life.

Further work is planned to better understand the impact on metal concentrations of overdosing heat-unstable wines with different bentonite products and any potential implications this may have on treated wines meeting regulatory requirements for export markets.

References

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Nicole Loveridge, Undergraduate Student, *Nicole.Loveridge@awri.com.au*

Tadro Abbott, Project Engineer, *Tadro.Abbott@awri.com.au*

Neil Scrimgeour, Senior Scientist

Jacqui McRae, Research Scientist

Eric Wilkes, Group Manager – Commercial Services