The Chemistry of Post-bottling Sulfides in Wine

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There has been a lot of discussion about wine closures of late, including some popular press coverage also. The re-emergence of the screw cap (some of us may recall it's first appearance – especially those of the Cold Duck era) has sparked a lot of interest in the performance of closures. Much has been written in the popular press on various aspects, such as the ability of wine to age under screw caps, the variability of the performance of corks, and the possibility of *reduced* characters under the near anoxic screw cap. Much (most?) of what has been written has little origin in science and more reflects popular beliefs. Further, very little of this material has been subject to any rigorous scrutiny. Consequently, popular opinion has often passed as scientific fact.

The chemistry of post–bottling sulfides in wine is in fact very interesting, at least to a chemist who makes wine! Further, the chemistry is reasonably well known and readily available if you know where to look. The first recorded documentation of the *reduced* character under screw cap was noted by the Australian Wine Research Institute[1] (AWRI) in February of 2003. There was no explanation for the mysterious sulfide character, but it did respond to copper fining. The AWRI seem still to be of the view that this is a winemaking fault to do with residual sulfides left in the wine at bottling despite warnings of a post-bottling reduction (and explanation) published by the author[2] in February 2002 and earlier popular press articles.

To understand the chemistry responsible for these post–bottling sulfides, we need to revert to redox chemistry. It is generally accepted that the traditional (cork) wine closure and a screw cap inhibit the ingress of oxygen post–bottling. In this regard generally cork is regarded as letting virtually no air into the wine.[3,4] The screw cap has been adopted on the same basis – as providing a near anaerobic seal.[5] Two observations have been made since the adoption of the screw cap. Firstly, the wines seem to age more slowly and secondly, there is a notable incidence of sulfides under this closures.[1]

If we can accept that the winemaker who doing a good job traditionally under cork (sulfide wise) is also doing an equally good job under screw cap, it is hard to apportion blame for these post-bottling sulfides on the winemaker; all that has changed is the closure. The winemakers who have adopted the screw cap generally have maintained that the cork was also an impermeable closure.[5,6] However, some permeability data for cork does exist in the form of MOCON (oxygen transmission) measurements as depicted in Fig. 1. It would be dangerous to equate these raw data quantitatively to wine, but they seem to suggest the ability for cork to permit some demonstrable oxygen ingress. If, in fact, cork does have an ability to transmit oxygen at a slightly higher rate than screw caps, then an explanation for the observations regarding ageing rates, and post-bottling sulfides exists via the differing redox chemistry of the two closures.

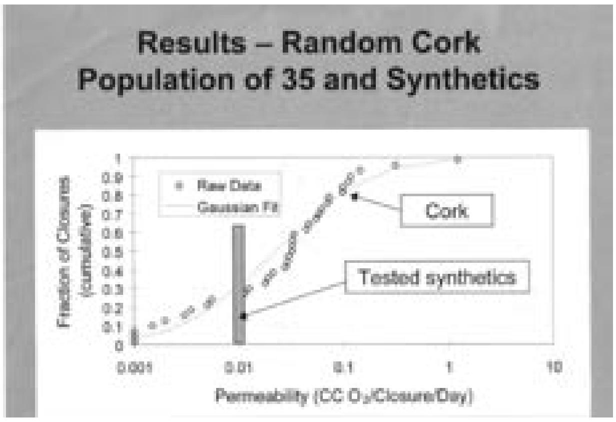
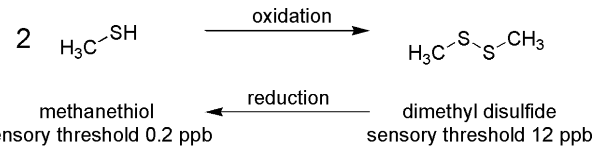


Fig. 1. Oxygen transmission rate for cork (measured by MOCON)

Wine can never be bottled completely free of sulfides. The ferment process leaves a sulfidic fingerprint, the composition of which depends upon the yeast strain and nutrient conditions in the ferment.[7] Usually, the principal components of these sulfides are the more noticeable H_2S and simple thiols such as methanethiol (MeSH). The lesser components tend to be simple dialkydilsulfides (such as dimethyl and diethyl), methyl and ethyl thioacetate (MeCOSR; R = Me or Et), and even some trisulfides. Fortuitously, H_2S and thiols respond readily to copper fining, depositing as the insoluble sulfides. However, the disulfides and thioactetates do not. As such, these components are commonly found in the bottled wine. Fortunately, these components also have a sensory threshold that is considerably higher than the copper treatable components. Threshold data vary depending on the source of the information, but typical values would be as MeSH: 0.2-2 ppb; DMDS 12-50 ppb; MeSAc 40 ppb. Unless a wine has a disproportionate amount of intractable sulfides (disulfides and thioacetates), the sensory effect of these is generally minimal, with typical values in the range of 5-10 ppb.

A common practice in wineries in response to the occurrence of sulfides is to *rack* the wine. This involves an aerative transfer from one vessel to another. Traditionally, this is widely practiced with red wine in barrel with the accompanying observation that the stink reduces. The process is usually repeated at regular intervals up until bottling.

The explanation for the disappearance of the odour can be found in the relatively easy oxidation of thiols to disulfides. Thus, for example, MeSH with a sensory threshold of 0.2 ppb is transformed into MeSSMe with a sensory threshold of 12 ppb. And the stink has gone. Or has it? Like many redox reactions the reaction is reversible. A common observation is that some months later, the wine needs racking again. Given that sulfides are formed at ferment, there is no likely source for the formation of new sulfides from wine that is separated from the lees (dead yeast). So the obvious explanation for the recurrence of the stink is the consequent reduction of the disulfide under a suitably low redox potential. This effect is depicted in Scheme 1. The evidence also shows that a typical redox potential scheme for racking is as depicted in Fig. 2.



Scheme 1

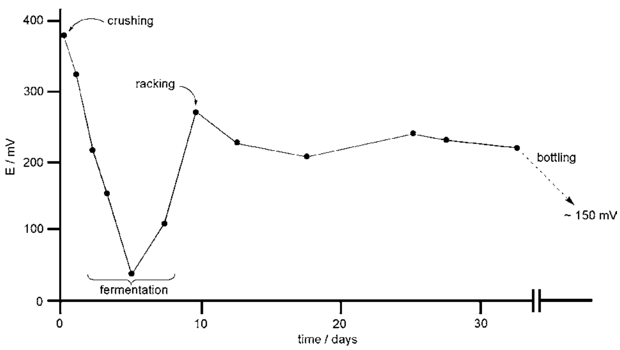


Fig. 2. Evolution of reduction potential during winemaking

So, we have a useful explanation for the occurrence of post-bottling sulfides for otherwise clean wine – *if the redox potential is low enough*. What is now needed is evidence of variation in the redox potential (dissolved oxygen) between the various closures. This can be gleaned from early screw cap development work such as that described by Bergeret *et al.*[8] These authors found that the redox potential under a tight sealing Al foil drops twice as far as other barriers, and the wine developed a *reduced* character. More recently, the AWRI have instigated a comprehensive assessment of the performance of various closures. This includes sensory analysis as well as basic chemical assays of, *e.g.* SO_2, that is known to interact with the oxidative products in wine, and is widely, but mistakenly, regarded as an antioxidant. It has no direct interaction with oxygen,[9] and its prime function is to bind with oxidative products such as aldehydes – which have a detrimental sensory effect on wine. In spite of the sometimes complex equilibria of the SO_2 in wine, a comparative measure of the respective levels in a wine gives some indication of the amount of oxidation that has taken place. The AWRI trials have generally focused on the *free* (or molecular) component rather than the total SO_2. The free SO_2 is the chemically active component. Some comparative data for the closures are shown in Fig. 3 and one can see that the screw cap (ROTE) retains higher levels of SO_2 than traditional corks, suggesting a lower amount of oxygen ingress. Altec also is a cork, but is of manufactured origin with an oxygen transmission rate quoted by the manufacturer as equivalent to ROTE. Interestingly, this information also shows a correlation between oxygen ingress and sulfide odour. Typically MeSH is attributed with a rubber character but there is also a strong relationship between the sulfide odour and SO_2. This is no coincidence, at least according to this author! It should be noted that AWRI claim that there is no causal link between the SO_2 correlation and the sulfide aroma.[10]

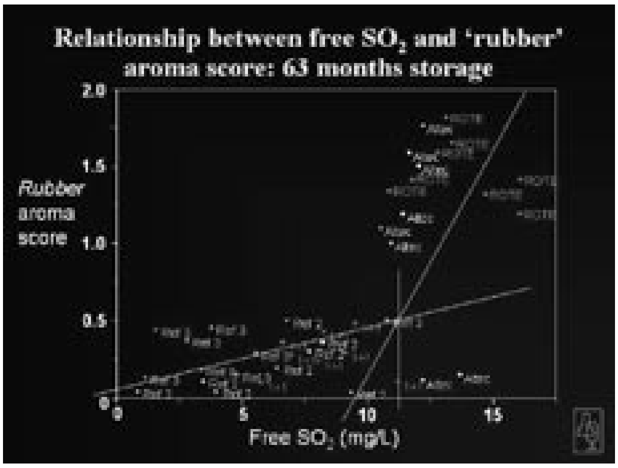


Fig. 3. Sulfide character related to closure type and SO_2

The kinetics of disulfide reduction have been described by Bobet *et al.*[11] and have been found to be first order with respect to disulfide and SO_3^{2-} (the requisite reducing agent for the disulfides), which is a component of the SO_2 equilibria. The time-scale for the complete reduction in a wine-like solution at pH 3.5 was *ca.* 2 years. This explains why these things are more prevalent as post–bottling phenomenon than in the winery, although the observant winemaker often notes that a wine in tank develops sulfide notes after copper fining. There is one further source of post-bottling sulfides via the thioacetate pathway. The hydrolysis of the thioacetates has been described by Rylander *et al.*[12] While the rates are higher for alkaline hydrolysis, acid hydrolysis also can produce measurable MeSH within a matter of weeks.[13]

So, via two independent pathways, one can observe and predict thiol accumulation in wine post-bottling. The reason why this is rarely seen under cork (see Fig. 3) is that the rate of oxygen ingress exceeds that of the thiol accumulation. Analysis of wine sulfide profiles post-bottling typically show an accumulation of disulfides at the expense of thiols and thioacetates.

This explanation of post bottling sulfides is still not generally accepted by those using screw cap closures; they prefer to attribute the problem to poor winemaking and pre-bottling sulfides. However, the chemistry tells us that the nearer we get to anoxia, *i.e.* the lower the rate of oxygen ingress under a closure, the more sulfide we are likely to encounter. This situation is graphically depicted from further AWRI results (Fig. 4). The ampoule could be considered completely anaerobic, with the screw cap near anoxic, and the cork slightly less anoxic.

So, in one of life's serendipitous coincidences, it would appear the humble cork has got the oxygen permeability just about right if we wish to avoid these post-bottling sulfides. Raising the permeability of the screw cap liner would have a similar effect.

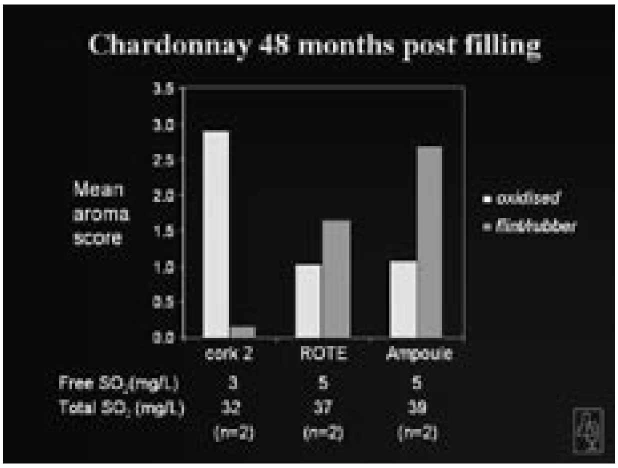


Fig. 4. Sulfide incidence related to closure type

An interesting aside to this discussion is the permeability of cork as depicted in Fig. 1. The data were derived by MOCON-type measurements that involve the headspace under a cork inserted into a bottle being swept into an oxygen-sensitive detector. These results suggest something like a 1000-fold variation in permeability, and some relatively high gaseous exchange rates for a supposedly near-anaerobic closure.[3] This variability has been widely reported by the screw cap proponents as evidence of the superiority of the screw cap as a closure. However, it is interesting to look at the data of Fig. 3 where the spread of SO_2 for any given closure type is very similar. Note carefully that *'Ref.2'* and *'Ref. 3'* that appear in this figure *do not* relate to the citations of this article but to that particular study for visual gradings of cork quality). The figure also tells us that the visual grading of corks has some control over the permeability as they seem to cluster as groups, *i.e.* 1 + 1, ref 2, ref 3 , Altec, etc., suggesting a variation in permeability better than 1000-fold, and comparable to the screw cap (ROTE). Further confirmation is found in the statistical data for free SO_2 reported in the 36-month results.[14] The standard deviations for these results are listed below where you will note the difference between ROTE and cork is minimal. Further confirmation of the predictability of the performance of cork is shown in the ability of the AWRI to predict[14] the SO_2 levels at 24-months from the 6-month data with an r^2 value of 0.89.

	1+1	Ref 2	Ref 3	Altec	ROTE	synthetic
SD(mg/l)	2	4	3	2	4	2

Furthermore, note the absolute values of oxygen transmission for the synthetic closures in Fig. 1. These were also under trial by the AWRI, but they ceased being of significance by about 36 months. The oxygen ingress rate was such that the wines had expired by this point. So, we know for sure that corks actually lie to the left of the synthetics in actual permeability, as their performance is still strong as seen by the 63 month data (Fig. 3).

All this information tells us that there is a considerable disparity in the actual performance of cork as a closure compared to the direct permeability measurement data. The reason for this disparity is not clear, but the author suspects it is connected to the various means of gaseous transport and specifically to diffusion kinetics vs pressure driven gaseous flux. The bottles in the AWRI trial were stored inverted at relatively constant temperature suggesting that the results are strongly driven by diffusion kinetics. It is interesting to note that the ref 3 corks in Fig. 3 are 38 mm while those of ref 2 are 44 mm in length. A longer diffusive pathway seems to indicate a higher degree of impermeability, although there is a grading difference further clouding the issue. The author would be interested in any further explanation readers may have to offer regarding the disparity in these results.

In closing, the closure debate has been a fascinating process for the chemist and winemaker to observe. Clear demarcations have occurred within the industry over choice of closure and writers have devoted miles of column inches to the topic; the winemaker's opinions on the mysteries of the chemistry above have passed as scientific fact. The process has, at times, had more in common with a fanatical religious belief than science. A few paraphrased quotes from a recent supposedly authoritative publication[10] on the subject serves to illustrate the point:

> H_2S can be reduced to mercaptans (p. 116).
>
> Thiols can be copper treated but mercaptans are more difficult. (p. 116/117).
>
> There is no SO_3^{2-} in wine (p. 101).
>
> DMS and DMDS are examples of mercaptans (p. 116)
>
> .. the permeation of oxygen thru the closure is negligible, if not zero*
>
> .. Corks have a variable permeability of 1000-fold.*

**These two quotes were by the same author in different publications 3 months apart.*

One conclusion from the recent focus on wine closures is that they will never be the same again. Cork manufacturers are for the first time learning about the technical aspects of the performance of cork, synthetic manufacturers are trying to reduce the level of permeability, and the screw cap manufacturers will need to consider a range of permeabilities rather than just focus on highly anoxic closures.

And the wines will be better off.

Acknowledgement

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4. NZSC Symposium, Nov 2004; NZSCI: www.screwcap.co.nz;

"the quantities of oxygen that normally penetrate into the bottles are negligible if not zero. Oxygen is not the agent of normal bottle maturation".

5. NZ Screw Cap Initiative web site: www.screwcap.co.nz;

"Screw caps are the ideal closures to exclude oxygen from the bottle."

"Q. The wine is a living breathing thing, and it needs to breathe through the cork, doesn't it?"

A. "(In every case) the answer is NO".

6. Stelzer, T., Winestar website, Feb 2005: www.winestar.com.au;

"Hence, it is clear that the oxygen permeability of the screw cap is essentially identical to that of the very best corks, and is in both cases negligible. The screw cap thus accurately replicates the maturation conditions provided by the very best corks."

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About the Author

Alan Limmer gained his PhD in Chemistry from Waikato University in 1982. Currently he is a Director of NZ Winegrowers and Chair of the Research Committee for NZ Winegrowers, and initiated the Hawke's Bay Charity Wine Auction that is now in its 14th year with over $1M raised for the local hospice. He is the owner and winemaker of Stonecroft Wines. Alan was awarded the ONZM in 2004 for services to winemaking and, in particular for his outstanding efforts in getting the Gimblett Gravels area of Hawke's Bay established.