

PART I

Do corks breathe? Origin of post-bottling sulfides

BY Alan Limmer

Redox reactions describe general principles and behavior of most wine reactions, both prior to and after bottling. Put simply, they are a series of interlinked reactions involving oxidation and reduction of various chemical species in a wine. Most wine chemistry is determined by this process.

In its simplest form, oxidation is the loss of electrons by one species, and reduction is the gain of electrons. Oxygen is not required for oxidation to occur, although it will frequently be the species that sets the “wheels in motion.” For every oxidation reaction there is an accompanying reduction, as these things come as pairs.

What is really happening is that the electrons are rearranging themselves into a more favorable order. This order is determined by the redox potential of the species. This measures their propensity to exchange electrons, either by donation [oxidation] or acceptance [reduction].

These reactions happen with a predetermined precision (although often in very complex systems) as dictated by the respective redox potentials of the species involved. The most likely reactions to proceed involve the species farthest apart in redox potential, and then the next, and the next, etc. There are further complicating factors which ultimately determine the precise outcome of these reactions in some cases, such as activation energies. But for the purposes of this discussion, we do not need to consider these factors.

Cascading effects

The redox system is really a series of interlinked chain reactions, or a cascading effect. For example, dissolved

oxygen, which is a powerful oxidant (as it causes species to give up electrons) in wine, in turn becomes reduced, because it is very happy to receive electrons. At this point, it should be clear that the term “reduced” has a rather precise meaning, which may have nothing specifically to do with sulfides (more on this later).

Once oxygen has entered the system, the primary redox reaction (electron exchange) will have occurred. This then permits a series of secondary and tertiary etc. exchanges to follow from this point, because the redox potential has been altered, and so a reshuffling of the hierarchy of possible reactants occurs.

The redox potential of a wine can be measured in a similar way to pH, although it is slightly more difficult. But the redox potential, at any point in time, reflects a wine’s history in terms of redox reactions, and where the wine is at the moment.

Generally speaking, wine in tank has a lower (more reducing) redox potential than wine in barrel, indicating the more severe anaerobic conditions in tank. The redox potential is lowest at the bottom of both containers — hence the significance of lees stirring. Wine in new barrels has a higher redox potential than that in used barrels.

Redox/Dissolved Oxygen

Perhaps a more simple conceptual way to look at this is to exchange the words redox for dissolved oxygen. Post-fermentation, a wine is in a reduced redox (DO) state, or more loosely, reduced. This is where a common misconception arises, because this does not necessarily mean the wine is exhibiting sulfide character. The display of sulfide character, at least primarily, has more to do with the pro-

duction of certain S-containing amino acids, in an effort to obtain satisfactory yeast nutrition.

Oxidation can also provide materials which may loosely be called reduced. But suffice it to say the wine will always contain sulfide precursors which will manifest themselves in various forms after fermentation, depending on the redox state.

Primarily, at least early on, a good deal of this reduced character can emanate from simple H₂S and a close relative, thiols (mercaptans). Thiols have the general form R-S-H where an H in H₂S has been substituted for an organic (Carbon) group denoted as R. R can be as simple as CH₃, the most basic organic (one C) group, or as complex as possible — leading to an array of really stinky thiols.

These compounds form the basis of skunk odor. The basic CH₃-S-H thiol is known as methanethiol and is a common constituent in wine sulfides. Simply put, thiols can be considered as substituted alcohols (CH₃-O-H = methanol) where S takes the role of oxygen. Methanethiol incidentally, is less reduced than H₂S; H₂S is oxidized to methanethiol.

Get the stink out

Given all this, we can see the error of using the “reduced” term to explain sulfide stinks, as in turn methanethiol can be oxidized to methyl disulfide (CH₃-S-S-H). This is yet another stinky reduced compound, and there is an almost endless array of these recombinations of sulfides that can form, all of which are in various states of oxidation (redox potentials) with respect to H₂S. No oxygen has entered the picture here, although it may have started the (cascading) process further up the line. But we are really referencing electron

transfers when discussing reduced and oxidized.

Oxidation of thiols to disulfides is relatively easy and can occur under mild oxidation conditions — such as O₂. This, in turn, is generally accompanied by a reduction in stink. Not necessarily because any sulfides have been removed, but because the sensory thresholds for sulfides shift markedly even with very small changes in their molecular structure.

For example, if a shift from methanethiol with a sensory threshold of 2ppb billion to methyl disulfide (MDS) with a sensory threshold of 50ppb occurs, immediately the character of the stink changed, and the intensity has reduced, because it takes more MDS to create a sensory impact than methanethiol.

Many, if not most, redox reactions are reversible, and the current sulfide status, as discussed above, simply reflects the redox state at that point in time. Also, as mentioned earlier, a series of cascading reactions occurs at this point, stabilizing the electron shift, which has occurred as a result of introducing oxygen at some point in the winemaking process, such as racking, filtration or bottling. Eventually, as the oxygen is adsorbed, and the reordering of electrons stabilizes, the wine will return to something near (but not quite) the original redox potential.

The response of the redox potential to an input of oxygen (at racking or bottling) is to initially incur a sharp increase in potential (towards the oxidative end). Curiously, this is shortly followed by a sharp dip in potential — below or more reductive than, the original potential. Eventually the potential will stabilize near the original point. During this process, a series of reducing reactions can occur again, and the MDS can become reduced to methanethiol. And the stink returns.

An important misconception regarding redox reactions is that oxidation can occur with impunity while the wine is protected with free SO₂. As discussed above, addition of oxygen sets up a cascade of redox reactions. It is a common misconception that free SO₂ scavenges oxygen and protects the

wine from oxidation. This is an incorrect assumption.

While SO₂ has important oxidative protection abilities, the “antioxidant” term is something of a misnomer, as it does not prevent oxidation. It merely acts as an intermediary in the redox process of oxidation and combines with some of the oxidation products, such as aldehyde, and effectively removes them from the system. In effect, the SO₂ must wait its turn in the redox queue. SO₂ has almost negligible direct interaction with oxygen in wine.

At this point, it should be obvious that redox reactions are critical to the sensory perception of a wine. General misuse of the term reduced when referring to the aromatic composition of wines has confused the situation. In other words, one can seriously oxidize a reduced (stinky) wine, but the sulfides will still be present in one form or another, as oxidized forms of the precursors, and may still stink, now or later.

Sulfide-free?

It should be obvious by now that S precursors are common in wine. Trying to produce a sulfide-free wine is like looking for the pot at the end of the rainbow. There are at least three good reasons why this is so:

1) Winemakers determine these things by sensory evaluation. All these compounds have different sensory thresholds, and at best, all one can determine is that the wine, in its current redox state is below sensory detection for sulfides. The threshold levels can vary widely from dimethyl sulfide at 50ppb to dimethyl trisulfide’s (DMTS) incredibly low 8pp trillion.

DMTS, which is reported as smelling of drains and dead animal, has been identified as a principal component of dead animal odor. The limit and variability of human detection suggests that there is always going to be sulfide precursors in a wine no matter how “clean” we think it is. The variable is going to be their behavior with varying redox potentials throughout the wine’s life cycle.

2) Some (if not most) of the sulfide forms in wine are unavailable for copper fining. The only ones which can precipitate with Cu(II) ion are the sim-

plest unsubstituted H₂S and the partially substituted thiols. All other variants do not combine with Cu(II). Depending on their compositional proportions, this mechanism is unlikely to remove every trace of all these sulfidic forms.

3) Most of these compounds are reported to have positive sensory effects at low levels (even DMTS), but become deleterious beyond those levels. Sauvignon Blanc is a good example where some complex thiols have an important positive sensory effect, but at the same time, the simple thiols (such as methanethiol) can spoil a wine. Much of the aromatic composition of a wine can be determined by S compounds.

Interesting also, the sensory attributes reported for these compounds change with their concentration. At low levels, a particular thiol may smell of peas or vegetal, and, at high levels, may smell of rotting cabbage, or worse. This may explain the wide variety of descriptors applied to individual compounds.

Getting screwed

Since introduction of the screw cap closure, a few unexpected aspects of the post-bottling behavior of wine have become evident. These require some explanation. The most evident of these aspects is the prevalence of sulfur-like odors (SLO) as noted in the Australian Wine Research Institute (AWRI) closure trials.¹ These characters are far more prevalent in, although not exclusive to, screw cap sealed wines.

Additionally, it is widely noted that the wines under screw cap develop differently and generally more slowly. If winemakers adopt the view that, in all aspects, the closures are identical in performance, other than taint aspects, then it becomes difficult to ascribe a reason for SLO under screw cap.

No explanation encompasses all aspects of variations in post-bottling performance of the two closure types. One scenario, which fits all the evidence available, would involve varying redox potentials (DO) between the screw cap wines and those under cork, which exhibit a lesser incidence of SLO. However, this does require sub-

scribing to the controversial view that corks permit ingress of some amount of oxygen.

A long held view, and particularly of late, is that corks have negligible permeability (more correctly referred to as oxygen transmission rate — OTR). This concept dates back to the early experiments of Ribereau-Gayon (1931) which demonstrated that sealing wine by cork, and the subsequent ageing process, was basically anoxic (or anaerobic) and the ageing process was one of reduction rather than oxidation. There have been more recent publications on this topic confirming this belief.²

The (re)introduction of the screw cap closure has been adopted on the basis that this is simply a further extension of the anaerobic ageing process and essentially no different in this respect to cork, albeit without the TCA taint, and perhaps more effective.^{3,4}

Explanations for the SLOs are varied and range from corks scalping any SLO, to the fact that somehow screw caps “magnify” the winemaking faults and corks mitigate them. If the scalping theory is accepted, which is unproven, although has a reasonable basis, then winemakers are left trying to explain why some corks do show SLO.¹ That some corks may scalp, and others not, seems problematic. Also, this does not explain the ageing difference between the closures.

If winemakers accept the explanation that screw caps somehow magnify the faults, and corks do not, the imponderable remains, how? In other words, this is no explanation for the differing behavior post-bottling under different closures.

Another explanation is that the wines were not clean before bottling and winemakers are urged to take more care. One could imagine, with the widespread noting of the occurrence of SLOs under screw cap of late, winemakers are, in general, taking more care than ever, and are certainly doing more copper(II) fining than ever before, as evidenced by the sales statistics of certain copper fining products (pers com). Yet, there are still significant incidences of SLO.

Chief judges at the 2004 Air New Zealand wine awards reported: “Too

many wines were showing sulfides under screw cap. Something to watch.”

Do corks breathe?

Although this may seem contrary to popular belief among some winemakers,⁵ let’s look at the evidence for the possibility that corks have a demonstrable OTR, that, in general, is higher than the near anoxic screw cap.

First, some bottles seem to develop faster than others. Assuming a single bottling, and common cellaring, the only variable is the closure.

Second, corks are about 85% porous (only 15% solid matter), and 85% air. That they seal as well as they do seems remarkable.

Third, it is a general observation that wine in magnums ages slower than 750 mL bottles, which in turn age slower than in 375 mL bottles. This suggests a relatively constant oxygen ingress between the two bottles producing different results in different volumes of substrate (wine).

Fourth, there are direct OTR measurements quantifying the permeability of corks. Two of these measurements are displayed in Figures I, II. Both these sets of results are largely in agreement with each other, although conducted by different institutions using different methodologies.

Solid proof

Figure I was produced from data derived from a study by Southcorp (Australia). The methodology employed is well developed and commonly used to test the porosity and permeability of other food packaging materials.

This data should not be translated as representing a quantitative assessment of oxygen ingress into wine. The following points may demonstrate the danger of this conclusion.

1) This flies in the face of the generally accepted theory of anaerobic ageing. Exchanging oxygen at volumes of upwards of 0.1 cc /day (or close on 36 mL per bottle per yr = 180mL air) hardly seems feasible.

2) If, in fact, there was a variation of 1,000-fold at these levels, individual wines would be unrecognizable. They would reflect the cork more than the wine. Yet, winemakers can generally agree on the character of a particular

aged wine. If not, tasting notes would be useless, and our drinking expectations of a particular wine would be entirely random, at odds of one in a thousand of having the same bottle twice.

3) Winemakers would not be able to distinguish between the ageing differentials of wine in magnums and in 750 mL bottles.

4) Note where the synthetics lie in Figure I, the bulk of the corks sit above this band. What is known about synthetics is that their permeability is excessive for all but very short-term wines. All synthetics tested in the AWRI closure trials passed away after about three years. From this, it can be safely concluded that cork’s performance under wine conditions as closures are, in fact, tightly bunched in the far left hand corner of this graph.

5) Data presented by AWRI predicted future (24 months) SO₂ levels under closures based on current six-month SO₂ levels, with a very high confidence, or predictability level ($r^2 = 0.89$).⁶ (If r^2 had equaled unity, there would have been a perfect correlation.) This could not happen if the corks were behaving as per the permeability graph. In fact, this evidence alludes to exactly the opposite conclusion, by the very nature of their high degree of predictability. Further, the AWRI closure trial demonstrates a relatively consistent spread of SO₂ results at 63 months for each closure type. The tightest band of SO₂ results belongs to the Altec composite cork, with the ROTE and other closures slightly more variable.

The 36-month data is listed below.⁸

	Free SO ₂	Total SO ₂ (mg/l)
ROTE	17 (4)	84 (5)
Altec	17 (2)	83 (3)
One + One	12 (2)	75 (4)
Reference 2 (44mm)	9 (4)	67 (9)
Reference 3 (38mm)	8 (3)	67 (9)

The Standard Deviation values () are a measure of the statistical variability of the data, and the closure performance results for each closure. The reference 2 and 3 corks show similar variation in free SO₂ results to ROTE, and about twice the variation in total SO₂, which is inconsistent with the spread of results obtained with the

OTR measurements. The conclusion by some, which has permeated from this OTR data, may be an unfortunate interpretation of raw scientific data extrapolated to a complex system.⁷

The tightest of the corks are possibly what some traditionally would generally call “good” (more on this later) corks, and may be near the permeability of screw caps. This incidence of very low OTR may be responsible for the low statistical proportion of SLO seen under cork,¹ and may be a better explanation than a variable capacity for scalping SLO.

Hair perming

The fact that wines may be exposed to some oxygen ingress is not contradictory with the general notion that the ageing process occurs at very low redox potentials. Once a wine is sealed, a natural drop in redox potential is expected.⁹

Any closure, except an absolutely faulty cork, or screw cap, will have the effect of reducing a wine’s exposure to air as experienced during general winemaking processes. If there will be small amounts of oxygen ingress via the cork closure as a reality, then it is possible to explain both the ageing difference between screw caps and cork and SLO incidences.

Clearly, a higher rate of oxygen ingress is going to lead to faster development of a wine, first because of the interaction of oxygen and the oxidizable substrates in wine, and consequent reduction in SO₂ level of the wine. Both of these aspects will lead to a variation in the redox potential of wine, with the higher oxygen ingress leading to an elevated (less reducing) redox potential.

An earlier section on redox behavior of sulfides explained the ready interchange between thiols and disulfides in wine, depending on the D.O. (basic chemistry). Disulfides are not able to be fined by copper(II), so not easily removed from wine. Under highly anoxic conditions, they can, and will, revert to thiols (SLO). (This is the theoretical basis of the ascorbic acid treatment in removal of disulfides in wine.)

What does this have to do with hair-perming? The answer is, everything. To perm hair, one first has to relax the

natural structure of the hair — which is determined by cross-linked proteins, joined together by disulfide bonds. These bonds are broken using a reducing agent. Then hair needs to be reset to the desired shape and fix it using an oxidizing agent — or re-instate the cross-linked disulfide bonds. In this case, the reducing agent is SO₃²⁻.¹⁰

The reaction is concentration-dependant (first order) on both SO₃²⁻ and disulfide.¹¹ This provides a very good explanation why there is a strong relationship between reduced characters found in the closure trial and free SO₂.⁶ Reduce the SO₃²⁻ (free SO₂) concentration by half, for a given wine, and the rate of SLO formation will be halved. But it will continue to form while there is disulfide and SO₃²⁻, just at a slower rate.

The disulfide concentration is also an unpredictable unknown in controlling the rate of SLO formation, and will vary from wine to wine. Either remove the SO₂ or the disulfide to stop the reaction from proceeding. Neither is particularly feasible. This reaction mechanism appears to explain all observations and experimental evidence to date on the incidence of post-bottling SLO.

With a very low OTR closure, the wine is on somewhat of a knife-edge in terms of oxidation and reduction. This is why corks have been so benevolent with respect to SLO. The low incidence of SLO seen under cork is not because some winemakers failed “Scalping 101.” Rather some chose to mimic screw caps while the rest were in the more oxidative phase.

The quicker the SO₂ level drops after bottling, the less chance there is of this disulfide reversion occurring. This would also explain why some bottles of wine (under cork) seem clean, and the next one slightly closed or “dirty.” Different rates of oxygen ingress.

The price for this benevolence under cork is that wine can suffer terminal oxidation at the other end faster than under screw cap (all things being equal). ■

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PART II

Do corks breathe? Origin of post-bottling sulfides

BY Alan Limmer

Anoxia = SLO (?)

Another dramatic illustration of the effects of very small amounts of oxygen, and their influence on sulfur-like odors (SLO) was demonstrated in the Australian Wine Research Institute's (AWRI) experiment showing relative amounts of sulfide character under three closures: glass ampoule, screw cap, and cork.

The ampoule is completely anoxic and demonstrates high sulfide levels, with the screw cap near anoxic and intermediate levels, and the cork sample showing almost nil, but higher oxidative levels. This also suggests the scalping theory is not the explanation for variation in SLO occurrence between screw cap and cork. The screw cap wine should have had the same amount of SLO as the ampoule.

By this chemistry, the nearer one approaches a state of anoxia, the more one can expect to encounter SLO. The redox chemistry of sulfides predicts this, and the excellent AWRI sensory work demonstrates the effect. Early development of screw cap barriers also encountered this problem.⁴ When a tight sealing aluminium barrier was used, the wine went reductive, but other barriers did not have the same effect. The redox potential under the aluminium barrier dropped sharply, about twice as far compared to the others.

Changing the barrier under the screw cap will alter these results. The AWRI trial results relate to the low ingress metal foil-type barrier.

This reduction effect is not, or should not be new to winemakers. How many times have you cleaned a wine up with copper(II) fining or filtration in preparation for bottling, only

to see it lose some of the vibrant varietal notes while stored under gas in tank? A further copper fining restores the original vibrant notes. This is a clear case of reducing redox potential producing more deleterious sulfide notes from an otherwise "clean" wine. There is no difference between this scenario and that experienced under screw cap — except you can't get at the wine again.

Clean wine status

This explanation has significant implications for the use of screw caps. First, it is incorrect to blame poor wine-making for all instances of SLO. Many, if not most, of the wines may well have been (probably were) clean at the point of bottling. But a definition of clean depends on the redox state of the sulfides.⁹ Scrupulous cleaning up of the copper-treatable sulfides is no guarantee against SLO. It requires the ascorbic acid/copper(II)/carbon treatment to remove disulfides (and then with limited efficacy).

Second, the commonly attributed benevolence of cork to these characters is actually a manifestation of the altered state of redox potential. This will be impossible to reliably replicate under screw cap without resorting to a range of permeabilities for these closures.

Third, the history and sulfide composition of a wine, plus a host of other antioxidant factors will vary from wine to wine, year to year. To predict which SO₂ level for a particular wine is likely to mitigate the effects of SLO is likely to lead to erratic and often, unfortunate results.

The alternative is to simply raise the degree of oxygen ingress. This will maintain the disulfides in their current form, and, in fact, oxidize any thiols into disulfides. (But the post-ferment

thiols [and H₂S] really should have been cleaned up beforehand).

It may well be time to look at a range of oxygen transmission rates (OTR)s for wine closures. Certainly they are going to be near the low (anoxic) end of the scale, but generally, likely to be above the current range of low-ingress screw caps.

The notion that every producer, and wine should subscribe to one minimal OTR-closure is like saying all wines have a particular style.⁵ Once there is enough OTR to cross the anoxic/sulfidic threshold, how much more ingress will be a stylistic choice. In the same way a winemaker chooses how much barrel ageing etc, and whether a wine is bottled more advanced or reserved as a style.

There are limitations at the moment, in choice, but closure manufacturers should be aiming to provide winemakers with a range of useful options, given this factor has such an influence on the post-bottling outcome. The lower the OTR of a closure, the more precise the wine parameters have to be met, regarding the competing oxidation/reduction to achieve a successful outcome. From that viewpoint, one could conclude it may be better to build in some latitude to mimic the cork's approach.

Available options

Figure II (courtesy of Oeneo Closures Australasia — formerly Sabate) shows a low OTR range for two closures — the P10 and P1. Oeneo Closures have the P1 and P10 in the market as Diamond (liquid CO₂ washed) and Reference (steam wash). The P1 has an OTR quoted as four times that of screw cap while the P10 is ten times that of the P1. There was under trial a lower grade of OTR — P0,

which was equivalent to foil screw caps. But this is not going to market. It did not score as well as P1 in sensory evaluation. The P0 formulation and OTR is the same as the one used for Altec corks in the original AWRI closure trial.

In the original AWRI closure trial, Altec corks scored as badly as screw cap for SLO.¹ This is further good evidence that scalping is not the issue regarding corks having less SLO than screw cap. The thing the Altec and screw cap have in common is their OTR (pers comm. — OeneoClosures). In fact, the OTR of the Altec appears to be slightly higher than the metal foil screw cap, but not enough to prevent SLO in the case of the trial wine.

The above information can help answer almost as many questions about wine closures and bottle development.

Do wines need oxygen to age?

No. Wine has no “need” for oxygen. The only part of the process which has a definitive requirement for oxygen is the increase in biomass of the yeast during ferment. Other than that, wine can be made completely anaerobically. But in practical terms, this is an impossibility and we have come to appreciate wine styles which have encountered some oxygen contact.

Also winemakers have come to learn and appreciate that certain amounts of oxygen, at certain points in the process, lead to beneficial outcomes — such as barrel ageing, micro-ox, etc. These are stylistic preferences to completely anaerobic winemaking. The same can be said for closures. The primary purpose of a closure is to reduce access to oxygen after the wine-making process has finished. In that respect, the screw cap is as near perfect as available. Almost there, but not quite.

The glass ampoule is the point where practice and theory coincide. Except, it demonstrates the highest level of SLO. Remember, the closer we move to complete anoxia, the more SLO will be encountered. The ampoule experiment is a good illustration of this.

Do red wines need oxygen to develop in the bottle?

Yes. If one wants a wine to evolve as per previous experience under cork. (This goes for white wine too).

To try and make one extremely low OTR that suits all wines is going to lead to variability of results not between individual bottles, but wine to wine, vintage to vintage. Winemakers, who have success under a screw cap one year, cannot necessarily expect the same result next vintage for the same wine.

If wines could be made guaranteed free of complex sulfides, and the bottle development was not expected, or required to follow the same pathway as the cork experience, then a totally anoxic closure may be the best solution. But this pathway puts severe demands upon the winemaking process. This is evidenced by the repeated occurrence of these SLOs, even when the winemakers seem mystified by their occurrence, having rigorously copper-fined the wine.

To require wines to be completely free of any sulfide precursors will place demands, which at this point in time, winemakers are unable to (and may not wish to) consistently achieve. The recently released report by the Australian Closure Fund also ran into the reductivity problem.² It is a wine specific condition, not a generic one.

The above information explains that the ageing process, post-bottling, is, in fact, one of oxidation rather than the commonly-held belief of asphyxia. It can be thought of in terms of a micro, micro-oxidation, at very low redox potential. But an oxidation, it is. Any oxygen ingress = oxidation, irrespective of SO₂ levels.³ In other words, a prime effect of the oxygen ingress is to mitigate the chemical effects of particular sulfide reactions, accompanied by a commensurate oxidative ageing of the wine.

Don't be shocked

This may come as a shock to winemakers who have held to the belief of the reduction mechanism for bottle age, and possibly a relief to those who have seen their SO₂ levels steadily diminish over time, until finally, the wine crashes. With this viewpoint,

controlling the oxygen ingress becomes a matter of significance, rather than aiming for total exclusion. In one of life's serendipitous coincidences, the humble cork has done a pretty good job, especially considering the age of the technology.

Do different wine types need different OTRs?

The simple answer is no. In general, cork traditionally (taint excepted) has done a pretty good job of ageing wine, then the median OTR and some range around that seems quite tolerable, for all wine styles. Winemakers generally have not chosen particular grades of cork for particular wines based on OTR. They are just as likely to use high-grade corks for all high-grade wines — be they delicate aromatics, or full-bodied reds. With equal success.

From this, it can be concluded that each style is capable of faring equally well within a reasonable range of OTR, providing the extremes are avoided. At the low OTR end, there may be some wines suffering from being tight, closed, faintly dirty (SLO), while at the other end, the wine will age faster than the norm. This would suggest that, as long as a wine is above the anoxic threshold, then the wine has no particular preference.

Certainly, by increasing the OTR to the upper acceptable end, a wine is going to develop faster and have a shorter shelf life. This may be useful in some circumstances. But, in practice, once there is enough OTR to cross the anoxic threshold (some safety margin may be useful), there is no need for more — other than stylistic preferences.

What the threshold value is may well vary for individual wines — which seems to be the case for the current low OTR screw caps. This level of oxygen ingress seems to be below the desired value for many wines.

Perfect closure

Theoretically for those subscribing to the anaerobic belief of bottle age, the perfect closure is the ampoule. By now, hopefully, many winemakers can subscribe to the fact that what may be required is an imperfect closure, as far

as permeability goes. But how imperfect?

The implications of striving for a closure to deliver as close to anoxic conditions as possible for bottle ageing, raises a number of interesting scenarios. The implications are significant, and require some thought beyond simply removing TCA.

The general conception that corks closest to anoxia are the best corks should be questioned.⁶ It may well be that wines sealed with these corks were the ones exhibiting some reduction character.¹ Given two bottles of the same wine, the one just beyond the anoxic end may be preferred.

The assumption that "good" corks mimic screw caps is just that, an assumption, which this author does not share. Sulfide in wine has traditionally been considered a fault because of the detrimental sensory effects on the wine. Which is why winemakers are trained to remove these with copper fining. Unless winemakers are about to change this view, any incidence of SLO under cork should be considered a fault as it should be for screw cap.

Assuming a wine has been cleaned up meticulously pre-bottling, how long would it take for SLO to show up if it was going to?

From one to 12 months. The reason behind the variable time issue we won't discuss here for space constraints. The literature suggests a time frame of up to 24 months, but in practice, it seems to eventuate faster than this.¹⁰ It would be a reasonably safe generalization to say that if it has not occurred within 12 months, it is unlikely to.

If it does occur, is it likely to go away?

Yes ... and no. No in the short term (several years), and yes, long-term (many years). Long-aged screw cap wines will have genuine cases where the winemaker does see the SLO character moderate.

Is it the wine or the closure that is at fault in the generation of SLO?

There have been many reports where categorical statements have laid the blame entirely on the wine(maker), that it is not the closure's fault. It could be considered the fault of the wine(maker) if wine was consistently produced and guaranteed free of complex sulfides or SO₂ (SO₃⁼). Neither of these options is particularly practical.

Conclusion

Production of complex sulfides in part, at least, is largely beyond a wine-maker's control. Further, they are not detectable by normal copper(II) fining trials, nor easily removed.

If the other view is adopted and the conclusion accepted that the SLO is generated by a lack of oxygen to mitigate the inevitable reaction between SO₃⁼ and disulfides, then blame should fall on the impermeability of the closure. By raising the OTR to mimic that of cork, the problem will diminish markedly, if not completely.

There is a further possible pathway to thiol accumulation which has not been covered above. Thioacetate (ethyl and methyl) production has been noted in the fermentation products of wines.^{7,8} Thioacetate (or thio esters) is also not treatable by Cu(II) fining and has the ability to hydrolyze to its respective thiols. Once hydrolyzed, the thiol products are indistinguishable from the disulfide cleavage process, and the end result is the same.

Thioacetate production has generally, although not exclusively,⁹ been linked to significant elemental S residues in fermentation.^{7,8} In some cases of post-bottling SLO, there will be wines almost certainly suffering from both causes of thiol accumulation. Only a specific chemical analysis of each wine's sulfide profile would provide a definitive answer as to the prevalent thiol precursors.

In a nutshell, the screw cap impermeability is encouraging a specific, unfortunate, post-bottling sulfide reaction (thiol accumulation), while cork's permeability discourages it. ■

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