Management of Wastewater pH for a Winery in Richland, WA

By
James McConnel
Mcconnel.jamesc@gmail.com

What you need to know

Acceptable pH Range:	**5.0-10.0**
Recommended pH Target:	**5.7**
Blue/Green or Gray Colored Wastewater is Safe for Disposal	
Dosage rates	
$NaHCO_3$	**8-10g/L**
$Mg(OH)_2$	**2.2-3g/L**
NaOH	**3-4g/L**

Problem Statement

City Regulations

The City of Richland requires that water released into the sanitary sewer system have a pH greater than 5.0 and less than 10.0.

Characterization of Wastewater

Major Operational Waste: Large volumes of waste containing high concentrations of organic acids, both in solution and as solid precipitate (lees). The pH is consistent with published values for the pH of wine, about 3.4 to 3.9. Traditional quantitative techniques for determining acid content (e.g. Titratable Acidity) are misleading, because of the presence of acids as solid precipitate. As acid in solution is neutralized, more acid is donated by the solid portion, with the result that much more acid needs to be neutralized than would be indicated by a sample of the liquid. So far, methods for accurate determination of overall acid content (solution and lees) are unknown to the author.

Minor Operational Waste: Small quantities of liquid waste; drips and spills; wine residue in equipment, tanks, pumps, buckets, pitchers, analytical samples etc. The pH is consistent with published values for wine. Quantification of the acid content seems unnecessary; neutralization of such small volumes requires a negligible amount of base. Given that the volume of this type of waste is so small and easily treated by dilution it may produce a false sense that this Minor Operational waste has no effect, as the volume of water used to rinse equipment is *often* but *not always* enough to produce a satisfactory pH. Nevertheless, monitoring of our discharge has shown that it *can* cause a drop in pH, when not properly managed.

Determination of Wastewater pH

Direct Measurement

Direct sampling and subsequent measurement by pH meter is the most accurate, and often a simple enough operation, when monitoring waste storage tanks, or occasionally checking the pH at the discharge point. However, it is not practical for Minor Operational waste. For instance, it would be unreasonable to require a sample every time someone rinses a bucket.

Anthocyanin Color as pH Indicator.

Luckily, red wine waste has some novel properties that can make the determination effortless. This is particularly useful when dealing with Minor Operational Waste. Specifically, red wine contains Anthocyanins, a class of compounds that can be used as pH indicators. Anthocyanins are known to be red or pink below pH 7.0, and blue, green or yellow above pH 7.0. Tests show our waste is consistent with this information, *see table at right*. This does not apply to white wine waste, because white wine does not contain Anthocyanins.

Color of Wastewater	
pH	**Color**
<6.0	Red or Pink
6 to 7	Grayish Purple
7 to 8	Blue/Gray
8 to 10	Blue or Green
>10	Yellow

Treatment Options

Dilution by Tap Water

Because our tap water is slightly alkaline (pH 7.6), it is possible to treat wastewater by simple dilution. Please note, it is the slightly alkaline nature of our tap water, not dilution in and of itself that increases the pH. Dilution with distilled water does not increase pH and in some cases can even cause it to decrease.

Tests have shown that to reach a pH of 5, beginning with untreated waste at pH 3.4-3.6, would require dilution by a factor of more than 60:1, possibly even more for Major Operational waste containing solids. Despite the enormous dilution factor required, this is often a viable method for treatment of Minor Operational waste because the volumes are so small that the amount of water required is not inordinate. For example, if a used bucket contains 10mL of wine, it only requires about 600mL of water to treat it by dilution. Simple observation of winery staff will show that the use of several thousand milliliters is common practice when performing this task.

Neutralization by Base

Several basic chemicals have been proposed for this use, they are:

1. $NaHCO_3$, aka: Sodium Bicarbonate, Bicarbonate of Soda, Baking Soda, Sodium Hydrogen Carbonate, saleratus, or nahcolite.
2. $Mg(OH)_2$, aka: Magnesium Hydroxide, Milk of Magnesia, or brucite.
3. NaOH, aka: Sodium Hydroxide or Caustic Soda

The following is a comparison of these chemicals. Please note, no source of $Mg(OH)_2$ was available for testing, as of this writing.

Buffering and Subsequent Dilution Effects in Treated Waste. Solutions treated with $NaHCO_3$ will have a buffering effect at pH 5.7 because of an equilibrium reaction with CO_2. Suppliers of $Mg(OH)_2$ claim that $Mg(OH)_2$ buffers at pH 9.0 in some sales literature, however I cannot find any supporting data or physiochemical reasons why this might be true. Tests have indicated, that if allowed to stand for several days, wastewater solutions treated (with NaOH) to a pH between 5.0 and 11.0 will move toward pH 5.7. This may be the result of an induced CO_2-$NaHCO_3$ buffering effect, but I cannot be certain.

Dilution by *distilled water* has been observed to decrease the pH of treated waste. Dilution by *tap water* causes an initial drop in pH followed by rising pH as the dilution factor increases. For clarity: waste was treated to a pH of 5.0 and then diluted. If *distilled water* was used, the pH would drop as the dilution factor increased. If *tap water* was used, the pH would drop to pH 4.5 and then begin rising again as more tap water was added. This suggests that it is the alkaline nature of our tap water that allows treatment by dilution. It also means that wastewater must be treated to a pH greater than 5.0 or a pH drop because of inadvertent dilution, may result in non-compliance.

Effect of Excess Treatment. $NaHCO_3$ will never produce pH values greater than 8.5, and therefore over treatment is not harmful. $Mg(OH)_2$ could potentially reach a pH as high as 10.5, however given that acids will also be present in the wastewater the likelihood of driving the pH above the acceptable limit is fairly low. NaOH can easily drive pH above the acceptable limit in cases of overtreatment.

Cost Effectiveness. Prices reported for neutralization chemicals, in the table below, come mainly from what information I could find on the internet. I make no guarantees regarding their accuracy.

Base	**Molar wt**	**Activity per mol**	**Activity per g**	**Neutralization Mass Relative to NaOH**	**Reported Unit Price (Est)**	**Neutralization Cost (Est)**

$NaHCO_3$	84	1	0.012	2.10	$1.00	$2.10
$Mg(OH)_2$	58	2	0.034	0.73	$3.00	$2.18
NaOH	40	1	0.025	1.00	$4.00	$4.00

Chemical Characteristics. Each base has different storage and handling requirements, as summarized in this table.

	$NaHCO_3$	**$Mg(OH)_2$**	**NaOH**
Maximum pH	8.5	10.5	15.5
Safety	Benign	Benign	Very Hazardous
Byproducts	CO_2 gas	None	None
Ancillary Requirements	None	Specialized mixing and storage systems	Protective Equipment
Notable Properties	Amphoteric: (neutralizes acids *and* bases) Buffers at: pH 5.7	Antacid and laxative	Deliquescent: (absorbs water from the air), this makes it difficult to measure out accurate quantities, as the weight changes.

Best Base

As shown in the table, to the right, $NaHCO_3$ and $Mg(OH)_2$ both have advantages. In terms of mass required $Mg(OH)_2$ is best and $NaHCO_3$ is worst. In terms of safety and risk of overtreatment, $NaHCO_3$ and $Mg(OH)_2$ are comparable, with a slight edge to $NaHCO_3$. $NaHCO_3$ and $Mg(OH)_2$ may be about the same cost depending on availability and price. $Mg(OH)_2$ may require special equipment, $NaHCO_3$ does not. NaOH is not the best base by any measure, including safety, cost, and dangers of overtreatment.

	Best Option
Safety	$NaHCO_3$ or $Mg(OH)_2$
Cost	*Variable,* $NaHCO_3$ or $Mg(OH)_2$
Mass Req'd	$Mg(OH)_2$
Special Equipment	$NaHCO_3$

Procedural Recommendations

Minor Operational Waste

I cannot recommend using any base other than $NaHCO_3$ in the following situations. The risk of overtreatment is significant.

Drips and Spills. Drips and small spills can usually be diluted effectively by hosing down the floor with plenty of water. If the spill is larger, or contains lees I would recommend sprinkling the area with $NaHCO_3$, and/or dosing the drain with a handful.

Rinsing Containers. If the tank, sump, bucket, etc. contains only a few milliliters of waste simply dilute in place, until the color changes from reddish to bluish, then release. If there is more than a little, try collecting the excess and disposing of it in the waste tank. If that is not practical, add a few handfuls of $NaHCO_3$ until the color changes. Less than a quarter of a cup is usually sufficient.

Pumps. Pump hoses can contain a significant amount of waste. Try filling a container with water and cycling it through the pump and back into the container, if it takes an excessive amount of water before the color changes, add a few handfuls of $NaHCO_3$. Do not release reddish or pink colored water, without confirming its pH.

White Wine Waste. White wine does not contain Anthocyanins which makes it more difficult to determine when it is safe to release. In addition to the suggestions above, it might be useful to add some red wine to the white waste for use as an indicator when cleaning using the preceding methods.

Major Operational Waste

Collectable Waste. It should be possible to collect most racking or other high volume waste into a storage tank for treatment and disposal. It is not necessary to watch for a color change in tank waste, if sampling is convenient. But do not release tank waste until the pH is confirmed; treat to a pH of 5.7 or greater.

When using $NaHCO_3$, add the dose before filling the tank, and mix the tank when it is half full. If you mix it when it is full, the CO_2 produced may cause it to overfill. When you mix the tank, be sure to stir up the bottom sediment, so that any un-dissolved base is available to the solution. I do not know of any special concerns when using $Mg(OH)_2$. I do not recommend using NaOH, but if you do, use appropriate protective equipment rinse off all equipment used, including the outside surface of the waste tank.

Uncollectable Waste. If it is not possible to collect waste in a central location, then in place neutralization, is possible with $NaHCO_3$. I would not recommend other bases for this purpose, if the amount of waste is not easily estimable, as the risk of overtreatment would be increased, be sure not to release waste without first confirming the pH. Treat to a pH of at least 5.7.

Base Dosage Recommendations

Target pH

I recommend a target pH of 5.7. When using $NaHCO_3$ the buffering effect at pH 5.7 will "lock in" the pH and make a subsequent drop unlikely. For other bases, a pH target would be somewhat arbitrary. However, dilution effects necessitate that it be well above 5.0, and since most solutions seem to revert to pH 5.7 eventually, this value would seem generally applicable.

$NaHCO_3$

In most cases $NaHCO_3$ seems to reach the required pH at a dosage between 8 and 10 g/L, more or less. It may take a few minutes to take full effect, allow 10-15min for the reaction before sampling. It is safe to use in any situation, and in any quantity desired. CO_2 production can be an inconvenience, but can be mitigated by controlled addition and mixing.

$Mg(OH)_2$

I have no experience with $Mg(OH)_2$, however, it should require about 2.2 to 3 g/L. I have heard reports that there are commercially available automated waste treatment units for wineries that use $Mg(OH)_2$.

NaOH

I do not recommend using NaOH, but it has been effective at dosage rates of about 3-4 g/L. If it is used, always use protective gear, rinse all equipment afterward, including the outside of waste tanks, and immediately rinse any exposed skin with plenty of *cold* water.

Although the preceding information is thought to be complete and accurate, it comes with no warrantee. Use at your own risk.