

## **The Formation of Lime Scale in Vineyard Drip Irrigation Systems**

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The precipitation and deposition of lime scale (calcium carbonate) in vineyard drip irrigation systems is one of the most common causes of system plugging and the associated loss of irrigation uniformity. The intent of this article is to describe the manner in which this precipitation occurs, thereby allowing for its prediction and the prevention of its contamination of your vineyard drip system.

Lime scale is the salt of two very common substances, calcium and carbon dioxide. It is commonly referred to as calcium carbonate, calcite or lime. The amount of calcium carbonate held in solution is dependent, to a certain degree, upon there being a small amount of carbon dioxide gas in equilibrium in the water. Cold water can hold more dissolved gas than hot water. In the vineyard, irrigation water tends to heat up in the black drip tubing, favoring the precipitation of scale. Calcium carbonate is also very polar, (the crystal has a “North Pole” and a “South Pole”, which creates an electromagnetic field), and will stack up like tiny magnets one upon the other to form large macro-crystals over time. The phenomenon of scale formation when water is heated is referred to as “the teakettle effect”, and it is common to find large flakes of calcite crystals in the household teakettle.

Scale formation in vineyard irrigation systems is a *chronic plugging problem*. That is, it slowly builds up over time, gradually restricting the flow through the emitter. The distribution uniformity of the irrigation system may be severely effected before any emitters are noticeably plugged.

To understand the mechanism for scale formation, we must look at different forms of carbon dioxide in water. There are five distinct forms of carbon dioxide that may be present in a vineyard drip irrigation system. These forms vary in the number of protons (hydrogen ions) with which they are associated, and are therefore dependent upon the pH of the water.

The first form is carbon dioxide gas, or CO<sub>2</sub>. The solubility of CO<sub>2</sub> gas in water is temperature and pressure dependent. Water under pressure can hold more gas than water in a vacuum. This is evidenced by the release of CO<sub>2</sub> bubbles when

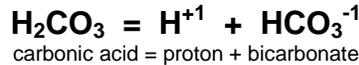
we open a bottle of “soda water”. When we heat up soda water, it releases even more CO<sub>2</sub> gas, because of the reduced solubility of gases at higher water temperatures (the teakettle effect).

The second form of carbon dioxide is carbonic acid, H<sub>2</sub>CO<sub>3</sub>, which is the combination of water and CO<sub>2</sub> gas.



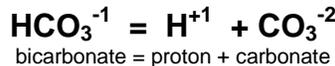
Carbonic acid does not retain the two protons as tightly as did the water, and these more liberated protons acidify the water and lower the pH. (pH is a measurement of the free protons in solution.) In fact, bubbling CO<sub>2</sub> through distilled water will lower the pH to around 4.5 because of the formation of carbonic acid, and the subsequent release of its proton.

The third form of carbon dioxide is the bicarbonate ion, HCO<sub>3</sub><sup>-1</sup>, which is carbonic acid that has lost the first of its two protons.

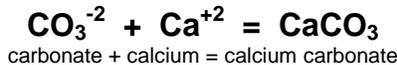


In water that is neutral (near pH 7), the bicarbonate ion is the predominant form of carbon dioxide.

The fourth form in which we may find carbon dioxide present in our irrigation system is as the carbonate ion, CO<sub>3</sub><sup>-2</sup>. Carbonate ions are formed when the bicarbonate ion, HCO<sub>3</sub><sup>-1</sup>, loses its second proton. This occurs principally when there is a relative lack of protons, characterized by a pH greater than 7.5 or 8.

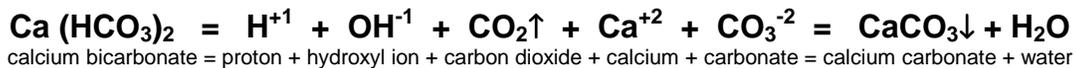


The fifth form in which we find carbon dioxide is calcium carbonate, CaCO<sub>3</sub>. This is lime scale, and it is typically formed when a calcium ion is able to come in contact with a carbonate ion. Because the calcium ion has a +2 ionic charge, it can satisfy the -2 ionic charge of the carbonate ion, forming the calcite salt.



If there are sufficient protons available in solution, the carbonate ions will most likely be in the bicarbonate form (HCO<sub>3</sub><sup>-1</sup>) and the calcium ions will be unable locate a carbonate ion to link up to and cause a precipitation.

There is another mechanism for calcium carbonate precipitation. This occurs during evaporation, and high concentrations of calcium and bicarbonate ions are created. Calcium bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ , is stable in solution as long as there is a slight excess of  $\text{CO}_2$  gas. The chemical equation becomes a bit intimidating, but what is happening is a bicarbonate ion, with the help of its neighbors, releases a hydroxyl ion ( $\text{OH}^{-1}$ ), which accepts a proton ( $\text{H}^{+1}$ ) from its neighboring bicarbonate ion to form water ( $\text{HOH}$ ). We are suddenly left with a water molecule, a molecule of  $\text{CO}_2$  gas that escapes into the atmosphere, a calcium ion and a carbonate ion. These latter two join to form a calcium carbonate precipitate (lime scale).



This reaction would be expected on the surface of an emitter, where evaporation can be quite high. It is also at the emitter where we often find a large pressure drop, which allows for the escape of  $\text{CO}_2$  gas. Another common location in vineyard drip systems where we find large pressure drops is in the throat of Venturi style injectors. It is not unusual to find lime scaling here as well.

So, we now know that by heating water and reducing its pressure we can favor the precipitation of lime scale. In the vineyard we send our cool, pressurized irrigation water through black hoses, and once the water heats up, we depressurize it through our emitters. How then, do we predict whether or not lime scale will be a problem and prevent it from eventually plugging up our drip systems?

In order to form lime scale, we need to have three conditions, the presence of carbon dioxide, the presence of calcium and the relative absence of available protons. The three factors are easily measured in the field.

The amount of carbon dioxide in solution can be measured by the ability of the water to absorb protons. If the water contains a great deal of carbonates and bicarbonates, the addition of free protons (acid) will combine with these to form bicarbonates, carbonic acid and  $\text{CO}_2$  gas. The net affect on the concentration of free protons (measured as pH) will be far less than if the water contained very small amounts of carbon dioxide. The carbon dioxide *buffers* the solution from large pH variations. This ability to absorb protons is termed **Alkalinity**. To determine the Alkalinity, a water sample is *titrated with acid* (acid is added drop by drop), until a certain pH is reached. The pH end point is usually determined by a chemical dye that turns color at around pH 4.5. Counting the drops of acid required to reach the end point allows us to calculate the total amount of carbon dioxide that was present in solution. This is termed Total Alkalinity, and is usually expressed as mg/l  $\text{CaCO}_3$ . Water with a Total Alkalinity over 150 mg/l

may cause emitter plugging in one season, if the calcium ions and pH are also favorable for scale formation.

The amount of calcium in solution can be estimated by performing a **Total Hardness** test. Hardness is a term used to describe the ability of water to form soap scum. The main ions responsible for precipitating soap are calcium, magnesium and iron. Of these three, calcium is the one we are most concerned with. Iron is typically present only in relatively small quantities. If it is present in larger quantities, it will probably demand a greater irrigation management focus than lime scale. Magnesium, on the other hand, does not form lime scale to the degree that calcium does. Magnesium carbonate is quite soluble, while magnesium hydroxide,  $Mg(OH)_2$ , is insoluble. Magnesium hydroxide precipitation can become a problem at higher pHs (above 8), but irrigating winegrapes with water this alkaline is unusual.

In the Total Hardness test, we add an indicator dye to a water sample that turns the water a wine red color in the presence of calcium and magnesium. We then titrate this sample with a chelating agent (EDTA) that complexes with the calcium and magnesium. (Complexing means combines with the ion, making it unable to precipitate out of solution.) When enough chelate has been added to complex all of the hardness cations, the indicator dye turns blue. By counting the drops titrated, we can calculate the Total Hardness of the water, usually expressed as mg/l  $CaCO_3$ . If your water contains a relative high percentage of magnesium as compared to calcium, the EDTA Total Hardness test will not be a good indicator of the potential to form calcium carbonate scale. Water with a Total Hardness over 200 mg/l could cause significant scale plugging in one season, given adequate Alkalinity and an elevated pH.

The third condition necessary for the formation of lime scale is the relative lack of available protons. This is easily measured as **pH**. In the field, pH indicator strips are most satisfactory. A pH approaching 7.5 or greater is cause for concern regarding scale formation.

Because of the volatility of the carbon dioxide chemistry, once we take a sample from our irrigation source water we begin changing the parameters that we wish to determine. Reducing the pressure of the water, mixing it with air during sampling and changing its temperature during storage will effect the equilibrium of carbon dioxide, potentially causing significant changes in pH, Total Alkalinity and Total Hardness. In fact, it is this volatility that presents us with the challenge of lime scale to begin with. For this reason, samples taken and sent to a laboratory for analysis several hours or even days later are of questionable value with regard to lime scaling potential. Field determinations of these parameters are quick and inexpensive. Field test kits for determining Total Alkalinity, Total Hardness and pH are available from catalogs and swimming pool supply stores.

The potential to form scale is limited by these three factors. If your water contains sufficient protons (below pH 6.5), the scale forming potential is negligible. If you have source water high in calcium and alkalinity and a low pH, the injection of a fertilizer that raises the pH, (ammonia for example), may cause the precipitation of calcium carbonate.

Another common occurrence is the addition of calcium to irrigation water that was previously low in calcium, but high in Total Alkalinity and pH, such as we may find in snowmelt surface water. In this case we are supplying the missing factor to form lime scale. Many vineyardists who begin injecting gypsum (calcium sulfate) into their drip systems find scale deposits in their emitters that did not form there prior to the calcium injections.

Whether or not the calcium, alkalinity and pH are conducive to forming scale is dependent upon a number of interrelated factors. One calculation that is commonly provided in laboratory water analyses is the **Langelier Index**, which takes into account these three factors as well as temperature and total dissolved solids. The Langelier Index expresses how far above or below the pH at which calcium carbonate would be in equilibrium in the solution, at a given temperature. A Langelier Index of +1.1, for example, indicates that the water has a pH 1.1 *higher* than the equilibrium point, and we would expect calcium carbonate precipitation. Of course, the amount of precipitate is limited to the amount of calcium and carbon dioxide present. On the other hand, if the Langelier Index is -0.5, the water is half of a pH point *lower* than the level at which calcite precipitation would be expected. This water would theoretically dissolve calcium carbonate (and corrode concrete pipes).

If your irrigation source water is conducive to scale formation, the question becomes, "How fast will it plug the emitters?" This depends upon the quantity of calcium and carbonates present, the amount of irrigation performed and the irrigation scheduling. The scheduling may influence the temperature of the water in the hoses, and how often the hoses are allowed to dry out. This is not to suggest that scale formation should play a major role in vineyard irrigation scheduling. There are better ways of dealing with lime scale plugging drip emitters.

First of all, if your source water is not conducive to scale formation (it has a negative Langelier Index), do not add anything that will change the equation to cause calcium carbonate precipitation. Avoid fertilizers that raise the pH of the water. Avoid adding gypsum to water that has a pH above 6.5.

If your source water is naturally lime forming, reducing the pH and the alkalinity with the addition of acid can modify it. Reducing the pH to around 6.5 will be sufficient. Many growers are seeking alternatives to acid injections, because of

the worker safety issues and potential damage to irrigation equipment and even the vines.

A class of water treatment chemicals known as **Scale Inhibitors** is being introduced to agriculture from industrial applications. Their chemistry varies, but they all serve the same purpose: to prevent the formation of large calcite crystals. Some do this by complexing the calcium, which renders it unavailable to the carbonate ion. Others do it by deforming the calcite crystal, making it difficult to form large, emitter-plugging crystals. Most of the products on the market are effective at preventing scale, and are generally cost effective compared with acid treatments.

A common method of dealing with lime scale formation is to allow it to form in the emitter and hoses, and periodically remove it with acid injections. Although this can be effective in the removal of calcite, there are some downsides to this practice. One is the fact that the distribution uniformity of the irrigation system is suffering between treatments. Another is the fact that higher rates of acid (at a lower pH) must be injected to *remove* scale than would be necessary in a continuous feed injection to *prevent* its deposition. A lower pH increases the risk of damage to the irrigation equipment and the grapevines. Another important factor is the worker safety issue. When irrigators are required to inject acid only once or twice per season, they may have failed to receive the proper training or refresher courses to allow them to safely handle the hazardous acid.

We feel it is better to treat scale formation in the vineyard drip system like you would treat powdery mildew on the vines...prevention is preferable to cure.

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