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Central Valley POSTHARVEST newsletter

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THE IMPORTANCE OF ADJUSTING YOUR WATER-CHLORINE pH DURING YOUR BRUSH-WASHING OPERATION FOR THE SAN JOAQUIN VALLEY STONE FRUIT INDUSTRY

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Why do we need to use chlorine in our stone fruit brush-washing operation?

The use of chlorine, or other approved water treatments, as fruit and running water disinfestations during the brush-washing operation is essential as brushing mildly damages the surface of the fruit. Thus, the proper use of chlorine during packaging can greatly reduce fruit infections during subsequent storage, transportation and retail management. However, while germinating spores and mycelium on the surface of the fruit are relatively easy to kill, resting spores are much more resistant to chlorine and pathogens growing inside the fruit (inside wounds or as quiescent pre-harvest infections) are shielded from the chlorine and not killed. Free chlorine levels of 25-50 ppm have been reported to kill most pathogens when used in clean running water in a brush-washing operation. Concentrations of 70-100 ppm of free chlorine are currently recommended for control of most postharvest pathogen spores in brush-washing systems, but some fungal pathogens are resistant to even these levels as contact times are typically too short. Studies by different groups illustrate both the relationship between chlorine concentration and exposure time on the disease killing rate and the variability in effectiveness depending on specific local conditions.

The most commonly used form of chlorine is sodium hypochlorite (NaOCl) although a few operators use chlorine gas (Cl_2) or calcium hypochlorite ($Ca(OCl)_2$) to a limited extent.

San Joaquin Valley stone fruit brush-washing operation pH water survey

During this season, we (Crisosto; KAC) surveyed pH on several commercial brush-washing operations. We found that pH ranged from 6.5-9.1. Most of the pH water samples were found to fall in a cluster of ~ 8.3. In general our well and /or tap water pH is ~7.4, but when hypoclorite is applied, the pH increases from 7.4 to 9.0 depending on chlorine dose concentration.

What is the effective form of chlorine in the water?

When either chlorine gas or hypochlorite salts (**NaOCl** or **CAOCl**) are added to the water, the following reactions occur**:**

1) $NaOCl + H_2O$ <-> $NaOH + HOCl$ (**hypochlorous acid**)
2) HOCl <-> $H^+ + OCl^-$ (**hypochlorite ions**) (high pH)
3) HOCl + HCL <-> $H_2O + Cl_2$ (**gas**) (very low pH; < 3.5)

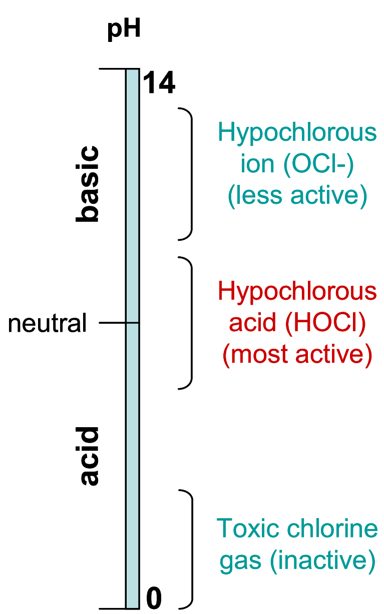


Fig. 1. Predominant chlorine forms at different pHs.

Of the many possible forms of chlorine, **hypochlorous acid** (HOCl) is what kills the pathogens in the shortest timeframe and, therefore, is the disinfectant dose to target (Reaction #1). We want to maximize the hypochlorous acid (HOCl) and minimize all the other forms of chlorine. In solution, the hypochlorous acid can disassociate to form **hypochlorite ion** (OCl^-) (Reaction #2). Hypochlorite ions, being slow-acting, are relatively ineffective against pathogens. At low pHs, most of the chlorine is in the hypochlorous acid form while at high pHs, most of the chlorine will be in the ion form. However, at pHs below 3.5 available chlorine activity is lost rapidly because another reaction is favored which produces toxic **chlorine gas** (Reaction #3). The irritating 'off-gassing' associated with hypochlorites is most typically from chloramines, a form of combined chlorine. Monochloramines will be abundant at pHs above 8.3. Therefore, maintaining a pH of around 7 will maintain about 80% of the chlorine in the hypochlorous acid (active) form with very little chloramine release and no concerns for the hazardous gaseous form (Fig. 2).

What is the relationship between pH and active or effective chlorine?

In running water, the desired available form of chlorine is hypochlorous acid (*active chlorine*), which is a much more effective bactericide than the hypochlorite (OCl–) ion. The degree of acidity or alkalinity of a solution as measured on a scale of 0 to 14 is known as pH. The midpoint of 7.0 on the pH scale represents neutrality; that is, a neutral solution is neither acid nor alkaline. Values below 7.0 indicate acidity; values greater than 7.0 indicate alkalinity. Although hypochlorous acid concentration is highest at pH 6.0, about 96% (Fig. 2), the best compromise of activity and stability is achieved by maintaining a water pH between 6.5 and 7.0. At very low pH, chlorine gas is released from water but this reaction is not significant above pH 3.5.

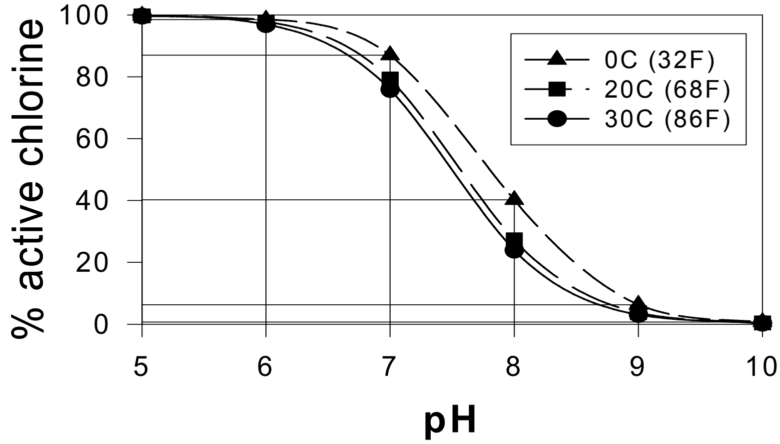


Fig. 2. Percent of chlorine in the active (HOCl) form at different pHs and temperatures.

Our preliminary laboratory test (Crisosto; KAC) indicated that high pH ($\geq$ 7.6) may induce higher white flesh skin burning discoloration, whereas low pH (< 6.0) may result in skin bleaching or burning. The susceptibility to pH looks to be cultivar dependent and the relationship is under detailed laboratory evaluation by our group.

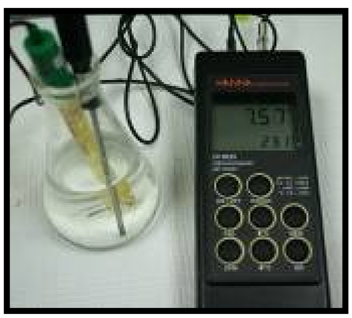
What is *total chlorine*, *free/available chlorine* and *active/effective chlorine?*

The terms ***total chlorine***, ***free/available chlorine*** and ***active/effective chlorine*** are used to describe the total amount of chlorine in any form available for oxidative reaction and disinfection. The term ***total chlorine*** refers to the ***free/available*** and ***combined chlorine*** that is present in water and still available for disinfection and oxidation of organic matter, including bacterial cells and fungal spores. It includes chlorine combined with ammonia or other less readily available forms of chlorine with weak antimicrobial activity such as chloramines **(combined chlorine)**. Chlorine may incompletely oxidize organic materials to produce undesirable byproducts in process water, such as chloroform/trichloromethane ($CHCl_3$) or other trihalomethanes that have known or suspected carcinogenic potential. At high pH, chlorine reacts with organic nitrogen-based materials to primarily produce mono-chloramines. Organic matter in the water will inactivate hypochlorous acid and can quickly reduce the amount of available chlorine. Chlorine which combines with organic matter no longer is readily active against pathogens but will still be measured by total chlorine testing kits. That is why it is so important to maintain the proper water quality. ***Free/available chlorine*** includes chlorine gas, **hypochlorous acid (active/effective)** and hypochlorite (Fig. 1). At high pH the free chlorine content can be high, but it will mostly be in the form of hypochlorite ion and so will be ineffective (very slow oxidizing activity). The same **free/available chlorine** content at lower pH will be much more effective. Thus, measuring free/available chlorine does not assure efficacy. It is crucial to maintain a pH between 6.5 and 7.5, preferably 6.5-7.0, so that the majority of the free chlorine is **active or effective hypochlorous acid** (Fig. 2). Thus, in order to know the sanitizing strength of one's chlorine solution, both pH and free/available chlorine must be measured.

How do we adjust pH?

Adding either sodium hypochlorite or calcium hypochlorite will increase pH, while adding chlorine gas will decrease pH. Chlorine must be continuously added to the water to replace chlorine lost to reactions with organic matter, chemicals, microorganisms, and the surfaces of fruits. After adding commercial chlorine, pH of the water must be adjusted to near 7.0 by adding either acid or base. One can determine the pH of water by using an electronic pH meter or color-changing paper indicator (Fig. 3). Food-grade muriatic (HCl), phosphoric, or citric acids are commonly used to lower pH while sodium hydroxide (lye) will raise pH. Typically, we may need to decrease pH of our hydrocooler water or running water after adding hypochlorites. To lower pH, one can determine the amount of acid to add by taking a sample of the water, adding acid to the sample until the pH drops to 7.0, and then multiplying the amount of acid added per gallon of sample by the total number of gallons in the tank.

a



b

Fig. 3. Portable electronic pH meter (a) and color-changing paper indicator (b) for fast measurement of water pH.

How do we measure effective sanitizer activity?

- Rapid test strips for measuring **total** and **available/free chlorine** (Fig. 4) can be easily purchased. Those that measure **available chlorine** within the desired range are needed because combined chlorine may give high readings in total chlorine kits. What we are interested in knowing is not how much sanitizer is present, but rather how effectively the sanitizer is killing microorganisms. Therefore, available/free chlorine measurements may be adequate when water is clean and pH is between 6.5-7.5. Swimming pool titration kits usually measure in the range of 1-5 ppm free chlorine. These kits can provide useful information if the water samples from the packing line are diluted with bottled distilled water (often 10-100 to 1) to the range of the kit prior to free chlorine testing.

Fig. 4. High range test strips for measuring available/free chlorine in the water are a practical way to monitor dosage. In combination with pH measurement, optimal active/effective chlorine (hypochlorous acid) will be present when pH is near 7.0.

What is an ORP system?

Since the main activity of chlorine and hypochlorite sanitizers is through oxidation, it is possible to measure their expected antimicrobial action by measuring the **oxidation-reduction potential (ORP)** of the water. This is measured in millivolts (mV) of electrical potential in the water. With an oxidation-reduction potential greater than 650 mV, most bacterial pathogens and a few sensitive fungal conidia will be killed on contact. In practice, by constantly maintaining the ORP level close to 725-800 mV, we can be assured that our brush-washing source water is of adequate quality without having to measure the amount of sanitizer in the water. For hydrocooler water or any recirculated water which has a somewhat higher ORP, 750-850 mV will be needed to reduce the survival of fungal pathogen spores in the water and limit the potential for cross-contamination. There are automated systems commercially available (Fig. 5) that monitor ORP and the pH of the water and inject sanitizer and acid as needed to stay in the proper range. This is a more direct way to monitor wash water decay control activity (**active or effective hypochlorous acid)** using a single value criteria than traditional measures requiring ppm available chlorine and pH. Sensors for measuring ppm free chlorine to monitor and control injection are available and may be an effective alternative to ORP. Both systems can be set up to provide electronic documentation of water status for record-keeping.

During this harvesting season, we monitored performance of an ORP connected two pumps (chlorine and muriatic acid) under a commercial operation. We were able to keep pH near 7.40, high level of free chlorine and ORP near 750-820 mv.

Fig. 5. Automated system monitoring the oxidation-reduction potential **(ORP)** and the pH of the water. ORP measurement is the most effective and direct way to monitor wash water sanitation activity.

Recommendations:

- Maintain pH around 6.5-7.5. The best compromise of activity and stability is achieved by maintaining a clean water pH between 6.5 and 7.0.
- Always maintain adequate separation between injection lines of concentrated hypochlorites and acids to prevent hazardous chlorine gas formation.
- Available/free chlorine measurements using a kit may be adequate when water is clean and pH is near 7.0.
- Check available/free chlorine and pH levels frequently. Installation of automated systems (ORP) to monitor and/or adjust active/effective chlorine and pH levels is desired to increase disease control effectiveness. Always have redundant hand-held methods of periodic testing of disinfectant levels to ensure automated systems and sensors are operating properly.
- Proper attention to water quality management will reduce potential for white flesh skin burning.
- Until more specific recommendations from on-going studies are available, maintain active/effective chlorine levels between 50 and 100 ppm (or 750-825 mV ORP) for ideal running water sanitation.
- For further information, please contact Carlos H. Crisosto at carlos@uckac.edu.

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FUTURE DATES

September 22-24, 2009. 14th Annual Fresh-cut Workshop. Fresh-Cut Products: Maintaining Quality and Safety. Davis, CA. Enroll On-Line.

16th Annual Fruit Ripening and Ethylene Management Workshop. February 25 & 26, 2010 at the Kearney Agricultural Center, Parlier, CA. For further information contact Carlos H. Crisosto at carlos@uckac.edu or (559) 646-6596.

First Winter Postharvest Short Course. February 21 to 25, 2011 at the Kearney Agricultural Center, Parlier, CA. For further information contact Carlos H. Crisosto at carlos@uckac.edu or (559) 646-6596.

Upcoming events are posted on the Postharvest Calendar at the Agriculture and Natural Resources, University of California (ANR) website at:
http://ucce.ucdavis.edu/calendar/calmain.cfm?calowner=5423&group=w5423&keyword=&ranger=3650&calcat=0&specific=&waste=yes

Information about upcoming events can also be found on the Postharvest Technology Research and Information Center website at http://postharvest.ucdavis.edu/:

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