The Use of
Chlorine Dioxide
IN POTATO STORAGE

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Introduction

Chlorine dioxide is a disinfectant compound widely used in multiple industries (e.g. wastewater treatment plants, wood pulp plants, swimming pool water purification, and vegetable/fruit process plants) as a general biocide. Chlorine dioxide can kill large populations of fungi, bacteria, viruses, and algae depending on the application rate and timing. This product is used in potato storage as an aid in the treatment of late blight (*Phytophthora infestans*)-infected tubers. It is only effective as a surface contact biocide and has no systemic properties. Check on current label status and recommendations prior to application to potatoes.

Chlorine dioxide chemistry is complex and differs from other chlorine-based compounds. Its primary chemical reaction is by oxidation, as opposed to chlorination, which is the case for hypochlorite compounds like bleach. Chlorine dioxide is a gas that is highly soluble in water. This property makes the use of chlorine dioxide relatively safe on food products. Chlorine dioxide is desirable for use in potato storage because it has low phytotoxicity, is not persistent, relatively safe, and environmentally friendly. However, there are several areas of concern in the use of chlorine dioxide: 1. The gas needs to be produced on-site due to chemical instability in transporting the product. Thus, this process called "activation" can be accomplished by activating dilute aqueous solutions of sodium chlorite with an acid to produce chlorine dioxide. 2. Formation of by-products, such as chlorates and chlorites, may produce undesirable residues on food products. 3. Consistent concentrations of chlorine dioxide are dependent upon temperature, pH of activation, and type of acid used to activate. 4. The release of gas to the air or "off gassing" of chlorine dioxide gas during the activation can be a safety hazard to personnel.

Chlorine dioxide should be used in conjunction with other good storage management practices including temperature and humidity control in order to be effective. It is not a curative compound and must not be regarded as one.

Principles of use

Current available chlorine dioxide products are Anthium AGP® (International Dioxcide) and Purogene® (Bio-Cide International). Anthium AGP® (EPA Reg. No. 9150-2) and Purogene Professional((EPA Reg. No. 9804-9) are 5% stabilized chlorine dioxide solutions and Purogene® (EPA Reg. No. 9804-5) is a 2% solution. It is important to realize the purchased products are not chlorine dioxide, but rather buffered solutions of sodium chlorite. Upon reaction with an acid (e.g. phosphoric or citric), the pH of the solution is lowered, and the production of chlorine dioxide occurs.

The chemical reaction required to produce chlorine dioxide (ClO_2) from a buffered solution requires the addition of a food grade acid to the Anthium AGP® or Purogene® product. With proper dilution the final pH of the applied solution should be in the range of 5-7. Without proper activation, very little chlorine dioxide is generated, and there is a reduced effectiveness as a disease suppressant, a potential for greater corrosion to metal surfaces, and possible undesirable residues on the potatoes. The presence of chemical residues on the tubers from the use of buffered chlorine dioxide products could impact the marketing of the potato crop.

Laboratory experiments have clearly shown the decrease in effective kill of disease organisms with non-activated chlorine dioxide compared to activated chlorine dioxide (Table 1). This information stresses the importance of fully activating the product, per label requirements, in order to generate a sufficient amount of chlorine dioxide to reduce disease organisms in storage.

Disease effectiveness

Limited research information is available as to the effectiveness of chlorine dioxide on late blight and other diseases in stored potatoes. Current research is ongoing at both the University of Idaho and North Dakota State University in evaluating the effectiveness and application methodology of chlorine dioxide.

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Chlorine dioxide is currently only labeled for late blight control. However, activated chlorine dioxide has the potential to kill several potato disease causing organisms such as *Erwinia caratovora* (soft rot bacteria) and *Fusarium spp.*, and *Helminthosporium solani* (dry rot and silver scurf fungi) at low concentrations as indicated by laboratory experiments (Table 2). These studies show the effectiveness of chlorine dioxide as a general biocide for surface or air-borne pathogens that could infect potatoes. Caution: There is limited information on how these concentrations relate to necessary application rates in a storage system holding multiple tons of potatoes.

Small-scale, simulated storage trials have shown chlorine dioxide to be effective in preventing rot in tubers inoculated with soft rot and late blight (Table 3). Chlorine dioxide appeared to be highly effective against soft rot and decreased the incidence of late blight. These studies were tightly controlled and did not include evaluations in a large potato pile where other factors such as the presence of debris and soil, the height of the pile, airflow, storage temperature, and humidity may influence effectiveness.

Application methods

Methods provided on the label for applications of chlorine dioxide include: a single application going into storage (400 ppm), an initial treatment (200 ppm), followed by either a continual treatment (50 ppm) or a periodic treatment (200 ppm). See below for dilution calculations to obtain the desired concentration.

- Single application applied as a low-pressure mist directly onto the potatoes going into storage at a rate of 0.5 gal of 400 ppm solution per ton of potatoes. This would be a method similar to application of Mertect-340F® (EPA Reg. No. 100-889). It is not recommended to combine chlorine dioxide with Mertect-340F®.
- Once all potatoes are loaded into the storage, allowable applications through the humidification system (dedicated cold-foggers, centripetal fans, or low-pressure lines installed in the plenums) include:
  - an initial application of 200 ppm AND,
  - a continuous application of 50 ppm for high-risk storage OR,
  - periodic applications of 200 ppm for unknown risk storage.
- Following initial applications, do not add more than 0.8 gal of Purogene Professional® or Anthium AGP® concentrate per 500 tons (10,000 cwt) of potatoes per month. Following initial applications, do not add more than 2 gal of Purogene® concentrate per 500 tons (10,000 cwt) of potatoes per month.

Table 1. Percent (%) reduction of viable Fusarium dry rot spores in laboratory tests with applications of activated and non-activated chlorine dioxide.

Chlorine dioxide (ppm)	Activated solution (% reduction)	Non-activated solution (% reduction)
0	0	0
50	100	10
100	100	21
200	100	17
400	100	20

Source: University of Idaho

Table 2. Laboratory tests examining activated chlorine dioxide concentrations needed to kill 50% (ED_{50}) of the disease organism.

Disease	10 minute dip (ppm)	Direct spray (ppm)
Erwinia carotovora (soft rot)	2	88
Fusarium sambucinum (dry rot)	12	52
Fusarium solani var. coeruleum (dry rot)	18	52
Helminthosporium solani (silver scurf)	122	4

Source: University of Idaho

Table 3. Effects of activated chlorine dioxide (200 ppm) on potatoes inoculated with soft rot (*Erwinia carotovora*) or late blight (*Phytophthora infestans*) at 65°F in simulated storage trials. Evaluated 12 days after application.

Treatment	Percent (%) of tubers with *Soft rot	*Late blight
No chlorine dioxide	30	73
200 ppm chlorine dioxide	0	38

*chlorine dioxide applied immediately after inoculation
Source: North Dakota State University.

- All potatoes treated with chlorine dioxide must be rinsed with potable water before consumption or processing.

Chlorine dioxide can be applied through the humidification system via evaporative cooling pads, but this practice may result in a greater deterioration rate of the resins binding the pads. Use of chlorine dioxide in this manner could result in a decreased life expectancy and may void the pad warranty.

When applying chlorine dioxide through the humidification system to stored potatoes, the application time should be a minimum of 1 to 2 hours to ensure good pathogen kill and pile infiltration.

Chlorine dioxide is moderately corrosive by nature. Higher concentrations and lower solution pH will increase the corrosiveness of the applied product. Chlorine dioxide is especially corrosive to soft metals such as brass, copper, and aluminum. Corrosion potential of such materials used in potato storage such as cold-foggers, fans, electrical wire, etc. must be checked and these items may need to be replaced more often. Not activating the product does not reduce the corrosion potential. Plastics, especially PVC, are not affected by chlorine dioxide and should be used throughout the application system if possible. Nylon tip nozzles are unaffected by chlorine dioxide.

Proper activation, dilution, and storage

The label requirements for both products state that activation (addition of acid to the concentrate) is necessary prior to the application to potatoes. Activation and dilution procedures for these two products differ and proper procedure for each is individually outlined.

Purogene® (2% chlorine dioxide)

Add up to 6 ounces of citric acid (or other food grade acid) (Fig. 2) to 1 gal of Purogene(concentrate. Make sure the pH is between 2 and 3 (use pH indicator paper or pH meter). After a minimum of 10 minutes, dilute the activated concentrate with water to achieve the following concentrations:

400 ppm: 2.6 fl. oz. of activated concentrate per gallon of water. Example: Add 0.6 gal (77 fl. oz.) of activated concentrate to 29.4 gal of water (final volume = 30 gal). This would treat 50 ton (or 1,000 cwt) of potatoes as applied going into storage at a rate of 0.5 gal of 400 ppm solution/ ton of potatoes.
200 ppm: 1.3 fl. oz. of activated concentrate per gallon of water. Example: Add 0.3 gal (38 fl. oz.) of activated concentrate to 29.7 gal of water.
50 ppm: 0.33 fl. oz. of activated concentrate per gallon of water. Example: Add 0.08 gal (9.6 fl. oz.) of activated concentrate to 30 gal of water. Apply according to label.

Purogene Professional® (5% chlorine dioxide)

Add up to 6 ounces of citric acid (or other food grade acid) to 1 gal of Purogene Professional® concentrate. Make sure the pH is between 2 to 3 (use pH indicator paper or pH meter). After 5 minutes, dilute solution with water as described below.

400 ppm: 1.0 fl. oz. of activated concentrate per gallon of water. Example: Add 0.24 gal (31 fl. oz.) of activated concentrate to 29.8 gal of water (final volume = 30 gal). This volume would treat 50 ton (or 1,000 cwt) of potatoes as applied going into storage at a rate of 0.5 gal of 400 ppm solution/ ton of potatoes.
200 ppm: 0.5 fl. oz. of activated concentrate per gallon of water. Example: Add 0.12 gal (15.4 fl. oz.) of activated concentrate to 29.9 gal of water.
50 ppm: 0.13 fl. oz. of activated concentrate per gallon of water. Example: Add 0.03 gal (3.9 fl. oz.) of activated concentrate to 30 gal of water. Apply according to label.

Anthium AGP® (5% chlorine dioxide)

Add 0.3 gal (38.4 fl. oz.) of 15% phosphoric acid to 1 gal of Anthium AGP® concentrate. Make sure the pH is 2.3 (use pH indicator paper or pH meter). Alternatively, add the necessary amount of a food grade acid to lower the pH of the concentrate to 2.3. Immediately, add this solution to 53 gallons of water. This makes a 1000 ppm 'working solution' to dilute to the following concentrations:

400 ppm: 0.4 gal (51.2 fl. oz.) of 1000 ppm 'working solution' per gallon of water. Example: Take 12 gal of 1000 ppm 'working solution,' add 18 gal of water (final volume = 30 gal). This volume would treat 50 ton (or 1,000 cwt) of potatoes as applied going into storage at a rate of 0.5 gal of 400 ppm solution/ ton of potatoes. For example, to treat 100,000 cwt of potatoes, 2,500 gal of a 400 ppm solution is needed.
200 ppm: 0.2 gal (25.6 fl. oz.) of 1000 ppm 'working solution' per gallon of water. Example: Take 6 gal of 1000 ppm 'working solution,' add 24 gal of water.
50 ppm: 0.05 gal (6.4 fl. oz.) of 1000 ppm 'working solution' per gallon of water. Example: Take 1.5 gal (192 fl. oz.) of 1000 ppm 'working solution,' add water to bring up to 30 gal.
Apply according to label.

It is important to dilute the activated concentrate immediately. If not, the chlorine dioxide will gas off, the product will be lost, and worker safety hazard will increase. Always activate and dilute in a well-ventilated area. Once the chlorine dioxide concentrate is activated and diluted it can be stored for up to 2 weeks. The non-activated concentrate can be stored for one year. In addition, dry powdered formulations are being evaluated for use in potato storage systems.

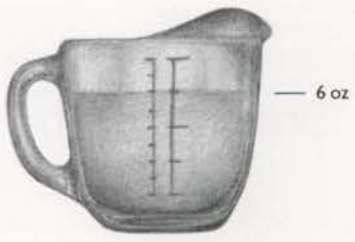

Figure 2. Activation requirement of 6 oz of citric acid or other food grade acids is equivalent to approximately 3/4 cup in a measuring cup.

Safety

Chlorine dioxide is a strong oxidizing agent. Personal Protective Equipment (PPE) must be worn during activation and dilution procedures. Equipment includes chemical resistant gloves, eye/face protection, and respirator. Other personnel who may come in contact with the treated potatoes must wear chemical-resistant gloves. This includes people sorting and inspecting potatoes. Chlorine dioxide can be very irritating to the eyes and respiratory tract. Some personnel may be more sensitive to chlorine dioxide, such as workers with mild respiratory ailments, and therefore exposure needs to be minimized.

Avoid exposure of the chlorine dioxide concentrate to sunlight, cold, and heat. Keep concentrated chlorine dioxide sealed until use. Activated chlorine dioxide solutions should be stored in light-proof containers. Once the concentrate is activated, do not replace the cap, but allow the solution to vent. If not properly vented, the container could explode due to a build-up of chlorine dioxide gas in the headspace.

Chlorine dioxide should not be stored or come in contact with acids, chlorine, bleach (hypochlorites), hydrocarbons, phosphorus, sulfur, organic compounds, potassium hydroxide, combustible/ flammable materials, and ignition sources.

If there is an accidental spill, in order to avoid potential fire danger, do not allow the solution to dry. Instead, flood the contaminated area with large amounts of water.

Always follow the product label for both application methods, rates, safety and container disposal. This publication is to be used only in conjunction with current labels and is not to be relied upon solely for information regarding the use of chlorine dioxide.

Additional information

To calculate volume of storage:
[pile length (ft) x pile width (ft) x pile height (ft)] / 2.5 = storage volume (cwt)

To calculate ppm of final solution:
Purogene® 2% chlorine dioxide solution —
(# of gallons of activated concentrate x 20,000 ppm) / # of total gallons = ppm of applied solution

Anthium AGP® or Purogene Professional® 5% chlorine dioxide solution —
(# of gallons of activated concentrate x 50,000 ppm) / # of total gallons = ppm of applied solution

Example: (0.13 gallons x 50,000 ppm) / 30 gallons = 200 ppm solution

Unit conversions:
1 gallon = 128 fl oz = 3.78 L = 3785 ml
1 fl. oz = 29.6 ml
6 oz = 3/4 cup

The listed products of chlorine dioxide are currently available under an emergency use exemption (Section 18). Future application use will depend upon successful registration for general use (Section 3).

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