

CHLORINE DIOXIDE USE IN PICKLING CUCUMBER HYDROCOOLER OPERATIONS

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ABSTRACT. Typical operating parameters for a chlorine dioxide generator installed on a hydrocooler (7560 L water capacity) for pickling cucumbers were ascertained. The recycled hydrocooler water (2-8°C) was maintained at 1.3 ppm chlorine dioxide to effectively control microorganisms. The rates of chlorite, hypochlorite, and hydrochloric acid use to generate chlorine dioxide were linearly related to the quantity of cucumbers hydrocooled for operating runs of 172 and 304 field boxes (705 L each, 20 bushels) intermittently hydrocooled over two 16 h periods. Use rates were 0.056 to 0.082 (chlorite), 0.052 to 0.078 (hypochlorite) and 0.022 to 0.029 (hydrochloric acid) kg/box hydrocooled. Materials cost for chlorine dioxide treatment was \$0.24 to \$0.29 per box. Optical density increased and total solids accumulated in the hydrocooler water in direct proportion to product throughput for both tests. **Keywords.** Chlorine dioxide, Cucumbers, Hydrocooling, Processing.

Chlorine dioxide (ClO_2) is a strong antimicrobial agent suitable for treating water used for washing, cooling, or fluming in commercial vegetable handling and processing operations. Research studies (Brackett et al., 1993; Costilow et al., 1984; Reina et al., 1995) have indicated that ClO_2 is effective at lower concentrations (1 to 5 ppm) than those recommended for calcium, potassium, or sodium hypochlorite (household bleach) which are employed at concentrations up to 200 ppm (Boyette et al., 1992; Brackett et al., 1993). In addition, the bactericidal action of ClO_2 is not affected by pH in the range of 6 to 10 and it does not react with ammonia to form chloramine compounds as do the hypochlorites (White, 1986). Chlorine dioxide is usually generated on site due to Department of Transportation regulations on its transportation and its cost for intermittent or seasonal applications in vegetable processing exceeds that of most other forms of chlorination (White, 1986).

Chlorination by any of the various forms of chlorine, including ClO_2 , is primarily for sanitation of the process water and non-porous equipment surfaces. It also limits the potential transfer of spoilage or toxic microorganisms from one batch of product to those subsequently processed. Chlorination has very little effect on the residual population of microorganisms on or just under the surface

of produce; the population of *L. monocytogenes* was reduced by about 2 CFU/g by dipping in a 200 ppm chlorine solution while dipping in water alone resulted in a 1 CFU/g reduction (Brackett, 1987). Similar levels of chlorine were also found to be ineffective in inhibiting growth of *L. monocytogenes* in lettuce (Brackett 1993). Bacterial populations in/on the surface of commercially hydrocooled pickling cucumbers were not significantly altered by chlorine dioxide at levels less than 5.1 ppm (Reina et al., 1995). Laboratory studies at 105 ppm ClO_2 were also found to be ineffective in reducing the population of microorganisms on the surface of fresh cucumbers (Costilow et al., 1984).

Since ClO_2 is effective in process water at only a few parts per million, it is preferable to other forms from the standpoint of minimal corrosive action on equipment and reduced potential for surface bleaching of produce. In addition, the lower concentration of chlorine residuals in process water and sediments may simplify discharge or disposal of waste materials. In some instances, depending on local regulations and circumstances, discharge permits of chlorinated waste water may be required (Boyette et al., 1992).

Extensive studies conducted under field conditions in 1993 utilized a large mechanical refrigeration, water curtain hydrocooler and automated equipment for generating and adding ClO_2 to recycled cooling water (Reina et al., 1995). Chlorine dioxide levels of 0, 0.95, 1.3, 2.8, and 5.1 ppm were maintained for 30 min test periods at a water temperature of 6°C. At levels less than 1.3 ppm, only marginal reduction (compared to 0 ppm) in microbial populations was noted; at 1.3 ppm, populations were reduced by 2 to 6 log cycles while higher levels did not provide proportionally higher reductions and were accompanied by an objectionable chlorine odor.

The current study deals with implementation of ClO_2 treatments over two 16 h operating cycles in a hydrocooler installation at a local pickle processor's facilities during the 1994 season. The objectives were to measure chemical use rates for generating and maintaining an effective control level of 1.3 ppm ClO_2 in the hydrocooler water, and to

Article was submitted for publication in February 1996; reviewed and approved for publication by the Food and Process Engineering Institute of ASAE in August 1996.

Paper No. BAE-96-01 of the Journal Series of the Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC 27695-7625. The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Research Service or the United States Department of Agriculture of the products named nor criticism of similar ones not mentioned.

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characterize system parameters under commercial operating conditions involving variable loading rates and intermittent use of the hydrocooler.

MATERIALS AND METHODS

HYDROCOOLER

The hydrocooler was a tunnel type, water curtain machine capable of transporting 705 L (20 bu) wooden field boxes of cucumbers (or other produce) through its 15.24 m length at an adjustable rate of 1.0 to 2.5 cm/s. A schematic cross-section with general operating characteristics is shown in figure 1. Cooling water capacity was 7560 L and was recycled at an approximate rate of 3850 L/min by a 352 kW (rated) mechanical refrigeration unit. During the cooling season the machine was flushed out and recharged each day. Water temperature on the discharge side of the hydrocooler (after passing through the cucumbers) was maintained at 5 to 8°C, depending on the rate of produce loading and its temperature.

CHLORINE DIOXIDE GENERATOR

Chlorine dioxide was generated by a commercially available generator (Rio Linda Chemical Co., Inc.) that mixed 25% concentration sodium chlorite (NaClO_2), 12.5% concentration sodium hypochlorite (NaOCl), and 15% concentration hydrochloric acid (HCl) in the proper ratios to produce ClO_2 . Mixing was accomplished by a vacuum drawn on the respective chemical feedstocks through a water driven venturi; the water- ClO_2 mixture was then injected into the hydrocooler cold water side of the refrigeration unit (fig. 1). The generator was equipped with an electronic on-off control system with sensor, located in the hydrocooler water return sump, set to maintain the ClO_2 level at 1.3 ppm. The generator was sized to produce 13.6 to 63.5 kg of ClO_2 per day.

CUCUMBERS

Cucumbers of various size and from several growing areas were hydrocooled during the green product intake

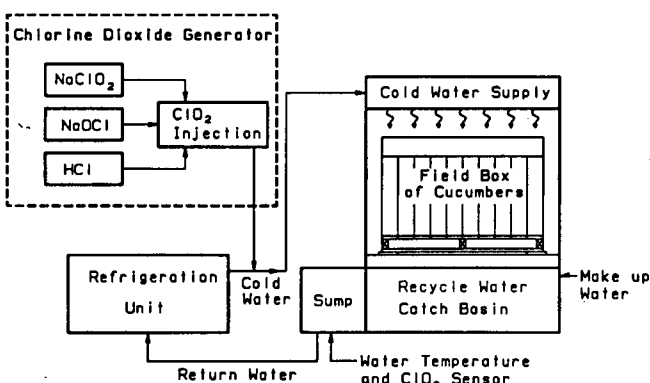
season to reduce their temperatures to 8 to 10°C for short-term storage (12 to 36 h) prior to packing. The loading rate and thermal load of the hydrocooler were quite variable throughout each of two test periods, depending on crop intake at the processing plant and ambient conditions. Some of the cucumbers had been washed prior to hydrocooling while others were not washed and were heavily soiled. This contributed to a widely variable demand on the ClO_2 generator since treatment of soil and wooden field box surfaces, in addition to the cucumbers, was involved.

MEASUREMENTS

Studies of this type are not readily adaptable to direct comparisons between treatments since temperature, quantity, size and condition of cucumbers hydrocooled could not be replicated over extended operating cycles. However, system parameters and responses for two operating cycles, each from about 8:00 A.M. to midnight on 9 June and 6 July 1994 (Test 1 and 2, respectively), were recorded to provide general trends. Observations were made every two hours for free and total chlorine in the hydrocooler water, the quantity of chemicals used by the ClO_2 generator, the number of boxes of produce hydrocooled, pH, optical density, suspended and total solids, water and air temperature, and the volume of make-up water added to the system.

Temperature measurements were made with dial thermometers at appropriate locations, chemical use was determined by weighing the respective 18.9 L containers with spring scales and water use was read from a flow meter installed in the make-up supply line which was activated by a float valve in the water return sump tank of the hydrocooler (fig. 1). Free and total chlorine were measured by a Hach Test Kit. Free chlorine values were multiplied by 1.9 to obtain ClO_2 concentrations as described in a 1993 study (Reina et al., 1995). Optical density of the hydrocooler water was measured at 600 nm with a Novaspec II spectro photometer (Pharmacia LKB Biotechnology). Suspended and total solids of the hydrocooler water were determined by standard methods as developed for wastewater measurements (Clesceri et al., 1989).

Microbial populations in the hydrocooler water were determined at the initial start-up of each test run and again after 3 h of operation for Test 1, and after 4 and 6 h of operation for Test 2. Bacteria, molds, and yeasts were enumerated by general procedures previously described (Fleming et al., 1984). Media for the various microorganisms included: standard methods agar (plate count agar, PCA, BBL Microbiology Systems) for total aerobes; violet red bile agar (BBL) + 1% glucose (VRBG) for total *Enterobacteriaceae*; (MRS) broth (Difco Laboratories, Inc.) + 1.5% agar + 0.02% sodium azide (MMRS) for lactic acid bacteria; standard methods agar (BBL) + 0.1 mg/mL of chlortetracycline HCl + 0.1 mg/mL of chloramphenicol for molds and yeasts, all as described in the 1993 study (Reina et al., 1995). All pour plates were duplicated and incubated at 30°C. Plates for yeasts and molds (YM) were incubated at room temperature (20 to 25°C). VRBG plates were read after 24 h and PCA and MMRS plates after 48 h. Yeast and mold plates were read after 72 h and confirmed after 120 h since both yeasts and molds were enumerated on the same plates, and molds



Typical Conditions:

- Cucumbers IN at ambient temperatures =>(20 - 35 °C)
- Cucumbers OUT at target temperature of 8 °C
- Total water capacity: 7560 L
- Circulation capacity: 3850 L/min
- Water temperature: 5 °C
- Chain Speed is variable: 1.0 to 2.5 cm/s (perpendicular to page)

Figure 1—Schematic of hydrocooler cross-section with chlorine dioxide generator, refrigeration unit and typical operating conditions.

Table 1. Variables associated with operation of chlorine dioxide generator and hydrocooler systems for Test 1 (9 June 1994)

Variables	Hours of Hydrocooler Operation									
	0	2	4	6	8	10	12	14	16	Total
Air temperature (°C)	21	22	25	26	26	25	23	23	22	X
Water temperature (°C)	3	2	3	8	2	2	4	6	7	X
Chlorine dioxide (ppm)*	2.09	1.14	2.09	0.57	1.33	1.33	0.76	1.17	1.52	X
Total chlorine (ppm)	1.50	1.10	1.35	1.40	1.90	2.30	2.35	2.60	3.25	X
Suspended solids (mg/mL)	0.015	0.043	0.040	0.025	0.110	0.118	0.109	0.178	0.188	X
Total solids (mg/mL)	0.313	0.430	0.490	0.486	0.711	0.802	0.800	0.990	1.15	X
Optical density (OD600)	0.048	0.081	0.103	0.100	0.298	0.357	0.351	0.429	0.455	X
pH	6.56	6.63	6.66	6.51	6.69	6.71	6.80	6.80	6.78	X
Number of 20 bushel boxes	0	12	8	0	43	18	5	53	33	172
Chlorite used (kg)	0.7†	2.3	1.6	0	2.1	1.4	0.5	2.3	1.8	12.7
Hypochlorite used (kg)	0.7†	1.8	1.1	0	2.1	0.9	0.2	2.3	2.5	11.6
Hydrochloric acid used (kg)	1.4†	0.9	0.2	0	0.2	0.9	0	1.6	0.5	5.7
Water added to system (L)	0	782	291	0	450	8	0	726	340	2597

* Chlorine dioxide values calculated by multiplying measured free chlorine concentrations by 1.9 (Clesceri et al., 1989). This probably accounts for chlorine dioxide values exceeding total chlorine in the initial periods.

† Initial amounts used during startup to bring the system up to set ppm.

frequently overgrew the plates after 72 h. Although yeast colonies were smaller at 72 h, the numbers did not change appreciably after 120 h, when they could be counted.

RESULTS

The physical parameters associated with two operating cycles of the ClO₂ generator equipped hydrocooler system are reported in tables 1 and 2 for two-hour intervals. In each case these results represent typical conditions in which the quantity (number of boxes) and frequency (time of day) of hydrocooling was dictated by the crop intake of the cooperating processor throughout the day. Start-up, with fresh water in the system, was around 8:00 A.M. and both tests ended at midnight some 16 h later.

The Test 1 data was for relatively moderate (by the processor's records) usage of 172 boxes while the Test 2 data represented a heavier throughput of 304 boxes. Neither test approached the maximum capacity of the system, i.e., 45 boxes/h, although the first two hours of operation for Test 2 (87 boxes) approached maximum capacity. In each test, there was two hours during which no hydrocooling was required. Ambient air temperatures followed an expected daily pattern for June/July while hydrocooler water temperatures were generally within 2 to

8°C with little relationship to ambient temperature or loading rate indicating that the refrigeration unit was more than sufficient for the thermal load.

Ideally, ClO₂ concentration should reflect the target value of 1.3 ppm. However, the on-off sensitivity of the controller, coupled with the fluctuations in demand for ClO₂ by the variable loading rate of system, resulted in a range from 0.57 to 2.09 ppm for both tests (table 1 and 2). The reported values are not necessarily extreme values since they were measured at two-hour intervals and represent discrete observations. Other measurements, made as spot checks during the two-hour intervals, were similar to the reported values with none being smaller than 0.57 or larger than 3.25. Total chlorine (residuals) in the hydrocooler water generally increased with time and the number of boxes hydrocooled; both tests were at relatively low initial values as expected and increased to 3.25 and 2.90 ppm, respectively, over the 16 h test periods. Hydrocooler water pH indicated only small variations over the test periods with Test 1 indicating an upward trend from about 6.6 to 6.8; the water in Test 2 was essentially constant at pH 6.5.

Chemical demand to generate ClO₂ for the system was obviously not time dependent but generally reflected the box loading rate as expected. For those periods without

Table 2. Variables associated with operation of chlorine dioxide generator and hydrocooler system for Test 2 (6 July 1994)

Variables	Hours of Hydrocooler Operation									
	0	2	4	6	8	10	12	14	16	Total
Air temperature (°C)	24	26	30	32	33	33	30	27	26	X
Water temperature (°C)	6	3	5	8	3	3	6	4	3	X
Chlorine dioxide (ppm)*	1.71	0.57	1.62	2.09	1.14	0.95	0.76	0.95	1.33	X
Total chlorine (ppm)	1.20	1.00	1.80	2.70	2.80	2.70	2.30	2.70	2.90	X
Suspended solids (mg/mL)	0.005	0.037	0.054	0.059	0.068	0.051	0.051	0.053	0.067	X
Total solids (mg/mL)	0.239	0.401	0.532	0.753	1.09	1.11	1.11	1.12	1.27	X
Optical density (OD600)	0.019	0.093	0.139	0.170	0.221	0.234	0.232	0.228	0.270	X
pH	6.48	6.50	6.49	6.49	6.43	6.50	6.50	6.56	6.49	X
Number of 20 bushel boxes	0	87	29	41	74	14	0	15	44	304
Chlorite used (kg)	0.5†	1.6	2.5	5.2	4.1	1.6	0	1.4	3.4	20.3
Hypochlorite used (kg)	0.5†	0.7	2.3	5.5	3.4	2.5	0	0.5	2.5	17.9
Hydrochloric acid used (kg)	0†	0.5	2.0	1.1	1.1	1.6	0	0	0.5	6.8
Water added to system (L)	0	242	238	38	378	450	0	19	253	1618

* Chlorine dioxide values calculated by multiplying measured free chlorine concentrations by 1.9 (Clesceri et al., 1989). This probably accounts for chlorine dioxide values exceeding total chlorine in the initial periods.

† Initial amounts used during startup to bring the system up to set ppm.

hydrocooling (from 4 to 6 h, Test 1 and 10 to 12 h, Test 2) chemical usage was not detected by the weighing apparatus which had a resolution of 0.227 kg (1/2 lb). However, during these intervals the electronic controller cycled on for several 10 to 15 s periods to maintain ClO_2 levels in the hydrocooler water. On the other hand, cumulative chemical use as related to the number of boxes hydrocooled suggest linear relationships as illustrated in figures 2 and 3. These data, which do not include the initial amounts to charge the system at start-up, were fitted to least squared relationships; the slopes of each data set were quite similar with chlorite use, at 0.056 to 0.082 kg/box, slightly higher than hypochlorite use of 0.052 to 0.078 kg/box. Hydrochloric acid demand was considerably less at 0.022 to 0.029 kg/box for the respective tests. All the correlation coefficients for these relationships (figs. 2 and 3) were 0.97 or higher.

Solids accumulated in the recycled hydrocooler water as soil and other particulate matter (suspended solids) washed off the surface of cucumbers or field boxes and as soluble constituents, primarily sugars, exuded from the cucumbers. These dissolved solids (calculated as the difference between total and suspended solids) accounted for 85 to 90% of the total solids (tables 1 and 2) for both tests. The buildup of total solids indicates that as each test proceeded with time and the number of boxes hydrocooled, the hydrocooler water became more contaminated. This process was mitigated, to some extent, by the fresh water added to the system (tables 1 and 2) to make up for water loss due to "wetting" of the product and evaporation. The rate of water addition was quite variable and was not correlated to hydrocooler use. Over the course of Test 1 (table 1), total solids increased 267% to 1.15 mg/mL for the 172 boxes hydrocooled. Data for Test 2 (table 2) indicates an increase of 431% for 304 boxes. Comparison of the rate of increase as a function of the number of boxes hydrocooled suggests a linear relationship (figs. 4 and 5)

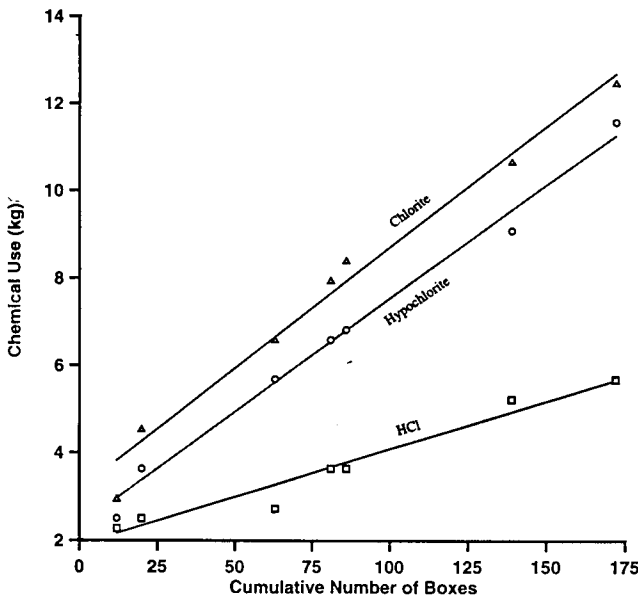


Figure 2—Chlorite, hypochlorite, and hydrochloric acid used to generate ClO_2 as a function of the number of boxes hydrocooled in Test 1. The respective slopes of the linear regressions are 0.056, 0.052, and 0.022 kg/box. Correlation coefficients are 0.98 or higher.

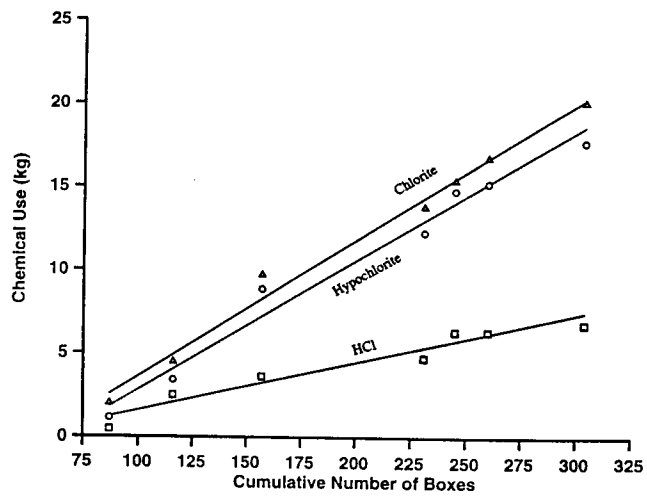


Figure 3—Chlorite, hypochlorite, and hydrochloric acid used to generate ClO_2 as a function of the number of boxes hydrocooled in Test 2. The respective slopes of the linear regressions are 0.082, 0.078, and 0.029 kg/box. Correlation coefficients are 0.97 or higher.

with slopes of 0.0046 and 0.0037 mg/mL box for the respective tests.

Optical density (figs. 4 and 5) also increased linearly with the number of boxes processed with the rate of increase for Test 2 over three times that for Test 1. Differences in the rate of increase of optical density are attributed to the state or condition of cucumbers entering the hydrocooler. Suspended and total solids, and optical density measurements confirm that as hydrocooler water is recycled it inevitably accumulates foreign matter in direct proportion to product throughput. However, "demand" or rate of use of the constituent chemicals to maintain 1.3 ppm ClO_2 did not increase as turbidity of the water increased.

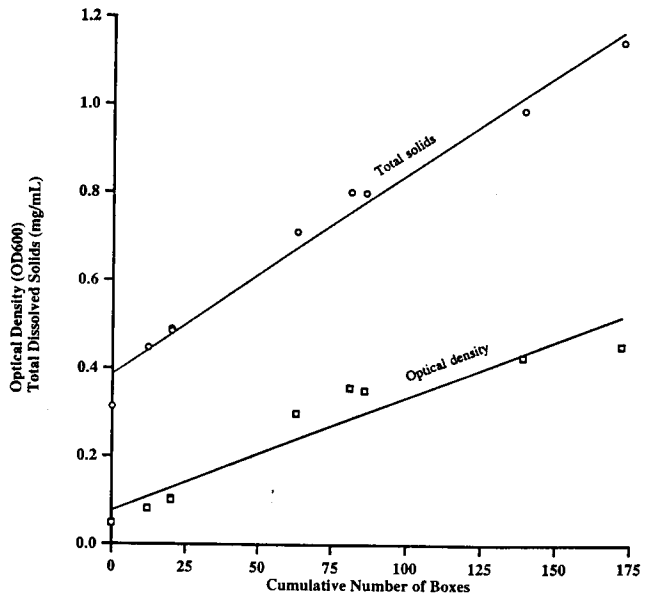


Figure 4—Hydrocooler water optical density and total solids as related to the number of boxes hydrocooled in Test 1. The regression line for optical density increases at the rate of 0.0026 units per box; total solids increases at the rate of 0.0046 mg/mL box. Correlation coefficients are 0.96 and 0.99, respectively.

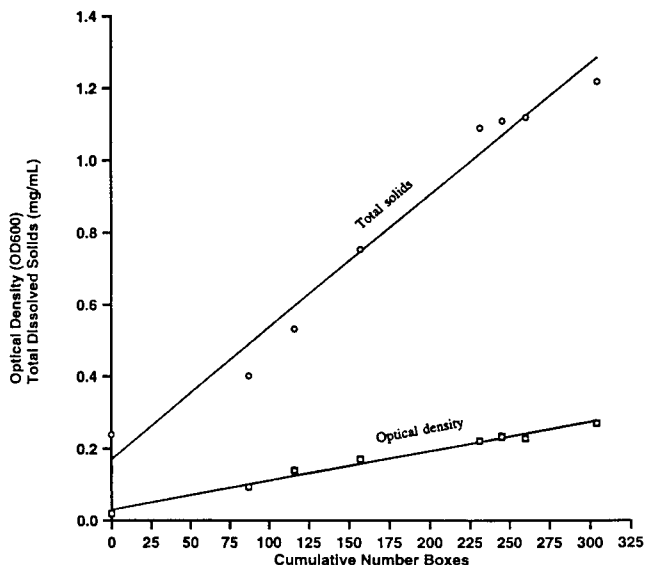


Figure 5—Hydrocooler water optical density and total solids as related to the number of boxes hydrocooled in Test 2. The regression line for optical density increases at the rate of 0.00082 units/box; total solids increases at the rate of 0.0037 mg/mL box. Correlation coefficients are 0.99 for both cases.

Microbial populations in the recycled hydrocooler water were determined at the initial start up of each test after the system was brought up to 1.3 ppm ClO_2 but before any hydrocooling. Enumerations were also made after 3 h of operation for Test 1, and after 4 and 6 h of operation for Test 2. The enumeration results (table 3) indicate that in each case the initial populations did not increase. It is also apparent that the numbers of microorganisms present were much lower — by several log cycles — than those observed in an earlier study with the same hydrocooler without ClO_2 present and reported as the last line in table 3 (Reina et al., 1995). Thus ClO_2 was effective in limiting the microbial numbers in the hydrocooler water.

DISCUSSION AND CONCLUSIONS

A build up of viable microorganisms in the hydrocooler water was not evident. Under the given operating conditions, chemical demand was observed to increase linearly with the number of boxes, or quantity, of cucumbers hydrocooled. Total solids and optical density in

Table 3. Microorganisms enumerated from cucumber hydrocooling water taken from the hydrocooling sump

Chlorine Dioxide (ppm)	Date Analyzed	Hours of Operation	Number (log CFU/mL)				
			Total Aerobes	Total Enterobacteriaceae	Lactic Acid Bacteria	Yeast	Molds
1.3	9 June 1994* (Test 1)	0	2.6	<1.4	<1.4	<1.4	<1.4
		2	2.1	<1.4	<1.4	<1.4	<1.4
1.3	6 July 1994† (Test 2)	0	3.5	<2.6	<2.6	<2.6	<2.6
		4	3.6	<2.6	<2.6	<2.6	<2.6
		6	3.4	<2.6	<2.6	<2.6	<2.6
None	1993‡	2	7.0	6.9	3.9	3.5	3.9

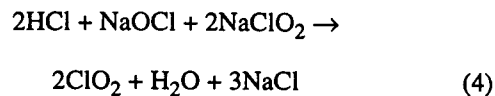
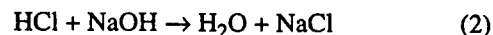
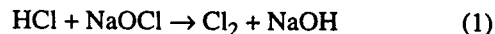
* Enumerated by the pour plate method described in Materials and Methods, where log CFU/mL of 1.4 is minimum number countable.

† Enumerated by the spiral plate method, using the same media as by pour plate, but log CFU/mL of 2.6 is minimum number countable, as described by Breidt et al., 1995.

‡ Data from a previous study (Reina et al., 1995) reported here for comparison.

the hydrocooler water also increased at rates that appear to be linearly related to the number of boxes hydrocooled. Thus the limiting condition for recycling treated hydrocooler water may be the accumulation of foreign material from the cucumbers and their containers.

The chemical components utilized to generate ClO_2 react as follows:



The overall reaction (eq. 4) was used to calculate theoretical usage of the feedstock chemicals. Theoretical (relative to HCl) mass use of the 12.5% NaOCl, 25% NaClO_2 , and 15% HCl should be 1.49, 1.22, and 1.00, respectively, as shown in table 4. Actual use ratios based on the total amounts used and the slope of the use rate per box hydrocooled (figs. 2 and 3) were calculated and are also reported in table 4. Obviously the ratios are not in agreement with the theoretical values which represent 100% efficiency of conversion by the generator.

Reduced efficiencies are attributed to several sources including frequent on/off cycling of the generator; each time the system came on the vacuum pulled on the respective chemical supply lines and the resulting flow of each chemical required a few seconds to stabilize at set levels. During these periods ClO_2 generation does not effectively utilize all of the three components. Flow rates are set visually by rotameter type flow meters which may also lead to errors in metering the respective chemicals since each time the system cycles the flow rate for each chemical may not return to the exact setting. Variations in water pressure or water flow rate to drive the metering system could also contribute to errors. In both tests, the use ratios (table 4) suggest that chlorite and hypochlorite was expended at a rate greater than theoretically required.

The direct cost of chemicals to maintain 1.3 ppm ClO_2 in the hydrocooler water based on the actual amounts used

Table 4. Feedstock use ratios (by mass) calculated from theoretical reactions and experimental data

Source of Ratio Calculation	Chlorite	Hydrochlorite	Hydrochloric Acid
	Hydrochloric Acid	Hydrochloric Acid	Hydrochloric Acid
Theoretical	1.49	1.22	1.00
Total quantity used — Test 1	2.23	2.04	1.00
Slope of Test 1 use rate (fig. 2)	2.65	2.43	1.00
Total quantity used — Test 2	2.99	2.63	1.00
Slope of Test 2 use rate (fig. 3)	2.69	2.50	1.00

and 1994 prices of \$3.52/L, \$0.77/L, and \$1.12/L for chlorite, hypochlorite, and hydrochloric acid, respectively, was \$50.41 for Test 1 and \$77.70 for Test 2. On a unit basis these values were \$0.293 and \$0.256 per box hydrocooled. Unit costs based on the use rate slopes in figures 2 and 3 were similar at \$0.240 and \$0.273 per box, respectively. These later costs do not include the chemical required to initially charge the system — \$3.97 and \$1.73 based on the initial chemical use values for the respective tests reported in tables 1 and 2. The wide variation is attributed to establishing stable flow rates in the generator system as noted above and the low resolution of the chemical weighing apparatus. Thus it appears that for hydrocooler installations of the current type, material costs for chlorination by ClO₂ generated from chlorite, hypochlorite and hydrochloric acid may approach \$0.30 per box.

Total chlorine in the hydrocooler water was not observed to exceed 3.25 ppm, well below the limits (4 to 5 ppm) of general use for processing fruits and vegetables to avoid detrimental bleaching or residual effects (Block, 1983). Stainless steel (Types 304 and 316) is not adversely effected at chlorine concentrations of 100 ppm if the pH is 7.2 (Bohner and Bradley, 1991). At the much lower chlorine levels and pH values (6.4-6.8) encountered in these tests, corrosion was improbable. However, copper heat exchanger tubes in the refrigeration system may be subject to corrosive action if longtime chlorine exposure exceeds 3 ppm (personal communication from Bradey Trane Service Corp., Greensboro, NC). Eddy current tests (Blitz, 1991) conducted by Bradey Trane Service Corp. on the refrigeration tubes following the tests did not detect pitting defects in the heat exchanger tubes.

Extension of the use of chlorine dioxide generators to other types of equipment — wet hoppers, flumes, washing and conveying machinery — should be considered. Control of microorganisms in process waters and general sanitation improvements appear to be likely. It is recommended that smaller, simpler generator units capable of accurate mixing be considered in order to extend the advantages of ClO₂ treatments to seasonally operated facilities.

ACKNOWLEDGEMENTS. This investigation was supported in part by a research grant from Pickle Packers International, Inc., St. Charles, Illinois. We thank Rio Linda Chemical Company, Inc. for the loan of the ClO₂ generator and their employees who provided advice and assistance. We thank Mt. Olive Pickle Co. for their assistance and contribution of hydrocooler facilities. We also gratefully acknowledge the technical assistance of David Vermillion, Laura Reina, Roger Tompson and Kathryn Crowley.

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