OZONE APPLICATIONS FOR COMMERCIAL CATFISH PROCESSING

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Introduction

Current methods of operation in Fish/Seafood/Poultry processing plants include the application of large quantities of chlorine in an aqueous solution, contacting the product directly by spray or submersion, in an effort to control bacterial growth in and on the meat during processing, and subsequently in the fresh meat marketplace; such bacterial content limiting the shelf life of the product (thus limiting shipping radius, storage in transit, export, etc.). The use of chlorine over the long history of this industry, has proven to be ineffective In controlling bacterial growth, resulting in poor shelf life, and inadvertently imposing a potentially harmful chemical on the consuming public.

As an example of the dangers of the use of chlorine, the United States Environmental Protection Agency (USEPA) has in the last two years formally taken a position against the use of chlorine in the public potable water supply due to fact that Trihalomethanes (THM's) are formed when the organics in these water supplies are joined with the chlorine injection commonly utilized in the United States for bacterial control. THM complexes have been proven to be of significant carcinogenic nature to humans; these compounds are very difficult to destroy or modify once formed in their natural state.

The potential for the formation of these compounds in this industry is significant (1), and may be controlled by the alternate use of another oxidizer other than chlorine (i.e. Ozone).

Use of chlorine is not an efficient method of bacterial control, or shelf life enhancement, thus additionally encouraging the use and application of another form of control (i.e. Ozone).

The presumption in this case is that the application of Ozone to the process meat industry would solve all of these current concerns, and provide a much greater degree of operational control and product quality.

Four operating entities were involved in this study: Mississippi State University, Matrix Design, Eco Resources,Inc., and Delta Pride Catfish, Indianola, Mississippi.

The goals, although specific, were aimed at a gathering of information and data, as well as the enhancement of the well being of a rapidly growing industry nationally.

Material and Methods

Delta Pride allowed two operating windows during the testing procedure. The first was in June of 1990, the second in July of 1990. Both were conducted within the plant at Indianola, in a real time environment.

The testing design was done cooperatively among all four parties. Delta Pride directed the locations of selection of the in situ meat for the tests. Eco Resources pro-

vided the bioprofile expertise, Mississippi State provided the knowledge of the industry and the goals that had to be accomplished during the testing period, and Matrix Design provided the process treatment design, kinetic projections, and equipment supply/operation during both testing periods.

Multiple levels of tests were scheduled, each encompassing multiple fish, and multiple stages of the processing plant. In Appendix A, the tests noted for the month of June show selected tests and their tracing of the processing procedure through the plant in an effort to find the most evident locations for application. The tests shown for July are reduplications of the June tests (to prove verification of the previous results), and new applications that were discussed among the parties after the initial June tests.

Fish were tested before processing in all cases; and after the selected process treatment. Swab tests were performed on each piece of meat (whole or fillet), to determine cell count (4 sq.In. sample area per sample of meat), with the respective swab recorded, video taped, iced down, and dry iced for shipment to a remote third party lab for results.

The equipment selection was difficult. The need was to provide equipment of a size and capacity necessary to oxidize the bacterial content, but not provide excess production capacity during the testing procedure (altering the results). Monitoring of the in situ process was of major importance.

Delta Pride desired to test the procedure first on the red water chiller, which was now being treated with chlorine. Because of the high organic content, an equipment selection was made that allowed for the inclusion of a unique microprocessor board within the Ozone production dielectric system. This board allowed the tests to be performed within a very narrow range of injection rate, constantly controlled by the microprocessor unit.

This unit would sense the condition of the feed air stream; sense the production system (quad dielectric); sense the discharge Ozone level and condition; and finally sense the uptake of the Ozone in the reaction vessel. All of these values were digitally preset for each bank of tests as shown in the data of Appendix A attached. At present there is only one manufacture of this equipment in the United States with its integral microprocessor unit.

In addition to the Ozone generator, compressed air, air dryer, and pumping units were provided. A 30 gallon test vessel (chiller vessel, reactor vessel) was provided to contain the water into which the Ozone and processed fish were placed. The Ozone was injected through a Kynar educator valve provided as a mixing device. All piping was CPVC, Kynar, or Stainless Steel.

Fish (25-30 pounds of whole fish per tank) were introduced into the test tank (held at a constant temperature range, 32 degF-38 degF), with the introduction of raw (untreated) tap water ice to maintain temperature (as in the present full scale processing plant), for a predetermined amount of time (several time frames, 10-12 min., and several concentrations of Ozone, 5ppm-12ppm were allowed). A predetermined amount of unfiltered recycle of the 30 gallon tank was allowed at each treatment level, as the level of Ozone injection was altered. A three part variable (digitally created, and controlled) was created for each test: Ozone quantity, time of retention, and amount of recycle. At no time was the retention more than that currently exercised by Delta Pride (20-30 minutes).

The goals were the reduction of bacterial count/content on the flesh of the fish being tested, and to increase the shelf life of the product. The scale or extent of the kill, and shelf life was unknown at the onset of the testing, but several assumptions were projected due to the nature of the Ozone injection process and its natural superior capabilities in the oxidation of organics (In direct contrast to that of products like chlorine). Previous testing has shown that the effects of Ozone on poultry were significant (2). Real time applications would be used in this case, not laboratory models, or controlled sequences. Attempts were made to duplicate the normal operating conditions of the plant, not laboratory controlled conditions; random fish samples, tap water (untreated),

atmospheric air feed, and nominal Ozone injection/contact time.

Peripheral areas of application would also be included in the testing procedures. Fillet treatment would be explored, attempting to lower the secondary processing recontamination of the meat for the prepared meat market potential. Equipment bacterial recontamination is a major problem in process plants, and the inclusion of Ozone treatment of both the equipment and the fillets would be preformed. Ice production would be treated to try and profile the improvements that would come from treatment of tap water with Ozone before ice making.

The first assumption was that the kill rate would be significant, in the whole fish category, and fillet category. This assumption would be defined by specific levels of cell count in each sample. Current (industry records indicate) levels suggest that the cell count of whole fish before exposure to chlorine is well above 100,000 (some have suggested that the count is at times above 150,000). The magnitude of the parallel problem in the poultry industry is detailed in multiple papers (2,3), recording the extent of the bacteria population typical in that industry. After exposure to chlorine the count in both Fish and Poultry can drop below the 35,000-50,000 level. Our goal was to better that tower bracketed number.

Our second goal was to increase the shelf life of the product significantly. Industry numbers indicate a current fresh fish shelf life of 4-5 days. Lastly, we would attempt to show the improvement in the ice cell count, as an application of fresh iced fish transport and marketing.

Ozone is unique. Production is accomplished with only small quantities of electricity, an electrical field, and a prepared air feed (either atmospheric or pure oxygen). No chemicals are required for production, Once produced, Ozone provides up to 15 times the killing power of chlorine solutions. In standard potable water applications, the use of Ozone can provide a four log kill in a fraction of the time as that required by chlorine under the same conditions. Some researchers have shown the comparisons between various disinfectants to be impressive when considering total kill rates of Ozone versus standard operational chemicals (4).

Ozone is a very unstable gas, artificially created (man made in this case) through the exposure of a dried, pressurized atmospheric air stream, to an electrical field. The "lasting character (half life) of Ozone (at temperatures above -32 degF) is very short. Half life is documented as less than 30 seconds. Oxidation takes place, kinetically, immediate on contact with the target subjects.

No after affects, or detrimental chemical/organic reactions are induced by the exposure of Ozone to water streams, or in human consumables. In fact, Ozone has been used in potable water treatment (for human consumption) since 1856. Today Ozone is widely utilized in the bottled water industry (Ozarka, etc.), soft drink industry (Coke, etc.), and beer and wine industry (Coors, etc.); FDA has authorized the use of Ozone in this industry as "Generally Recognized as Safe [-Technology], (GRAS).

Ozone has been added to the USEPA Best Available Technology (BAT) list for potable and waste water applications for the elimination of chlorine in the water systems of this country. Recently the largest Ozone system in the world was installed for the City of Los Angles potable water supply (>three billion gallons per day production); a second system was recently designed and is currently under construction for the City of Ft. Worth, Texas for its potable water supply.

Chlorine has been identified as older and less efficient technology. The USEPA has confirmed that chlorine (utilized as a bacterial control agent) in public and private water supplies causes the formation of THM complexes that are extremely carcinogenic to humans once ingested. The formation comes from the exposure of organics in the surface water sources to the raw chlorine feed that is intended to destroy the bacterial content of the water source, and to provide a residual of killing capacity control during the distribution of the water to the end user. Typically 5 ppm of chlorine is added, then the water is aerated to remove the overage of chlorine content, retaining at least 1 ppm for

distribution. Even at these tow levels of injection, the creation of these THM complexes is typical.

The USEPA is now directing public water districts across the United States to stop using chlorine in waste water discharges (thus eliminating the build up of the possible reaction/creation of THM's in the surface water that is eventually used as potable sources), substituting Ozone (or other BAT's), or the use of chlorine and a chlorine removal system prior to final discharge into the receiving surface water stream.

Chlorine has always been the oxidant of preference. Its reaction time was slow, as indicated by the typical retention time at a potable/waste treatment plant of 20-30 minutes, before release, Kill rates were eradicate. The chemical itself was a danger to the workers and excesses of injection were of major consideration to the users (due to the human danger involved). Preference for chlorine use is now changing.

Ozone has none of the potential dangers displayed by chlorine. Benefits are many, including the increased efficiency (kill rate, four log kills are typical), and lack of danger to operators, and users alike. The costs are low, due to the lack of depletables (other than the electricity required for operation).

Results

As shown in Appendix A, the results of June and July confirm that the use of Ozone (as configured in these tests) is very effective in bacterial control at the Delta Pride facility. Levels of kill fell generally below the 1000 cell count level for June, and well below the 200 level in July; considerably below historical operating standards in the industry.

June test results (see plate #I) were indicative of our desire to test a wide variety of sources, with some narrowing to be expected for the next set of tests in July. Effectiveness of the June tests were generally impressive, especially in the whole dressed category (<5000 w/o Ozone, <932 w/Ozone), and the fillet category (<5000 w/o Ozone, <120 w/Ozone). Results of the pre Ozone tests show the values of cell count to be greater than 5000. This oversight was corrected in the July tests to show the true values (although the total number of tests were not as comprehensive).

Fillet contamination was shown to be coming from the fillet operation, and its inherent recontamination potential. Fillets that came off this line evidenced very high levels of count, even with the multiple chlorine spray nozzles that are an integral pan of the machines utilized for this operation. Application of Ozone at this stage of the process proved very effective in the June tests (>75% reduction over conventional treatment).

July proved that the results obtained in June were capable of replication, and could in fact be improved upon once the base data of June was reviewed (see plate #2). July concentrated on the pure Ozone chiller results on whole fish (<80 count), fillet treatment with Ozone (<190 count), ice made with and without Ozone, and shelf life improvements.

Whole fish results ranged from 10 to 80 cell count over multiple whole fish swab tests. All fish tested were deheaded, gutted, and skinned. The fish (six each test, in the 5-6 lbs. size range) were placed in the Ozone chiller tank for the allotted time frame, and Ozone concentration. Fillets were then made (automatically) of these ozonated whole fish.

Fillets were cut from the whole ozonated fish, but without ozonated spray on the fillet machines, without ozonated pretreatment, and without ozonated ice for packing the whole fish. Fillets created from this flow schematic resulted in low cell counts of 120-190. Fillets without Ozone treatment (but with conventional treatment) ranged from 7,500-85,000 cell count (see plate #3).

Fillets were selected from the Ozone treated groups, set aside for a shelf life test, and subsequent taste testing by inplant quality control personnel. The fillets were Iced (with tap water ice) and kept at 34 degF and tested for smell, appearance, and firmness.

Taste tests were performed at day one for any traces of Ozone or off flavor due to the change in treatment. The taste testers were not aware of the change in treatment, and no indication was given as to any off flavor, or degradation in quality over conventionally treated fillets.

Shelf life was shown to be 14 days with Ozone treatment (see plate #4). This compares with 4-6 days for conventional treatment of iced fillets. On the fourteenth day, an appearance of odor was present. No reozonation of the fillets was done after the initial treatment on day one; this in contrast to previous studies that showed nominal changes in shelf life (5), were obtained with large quantities of Ozone exposure. Shelf life does vary according to fish type, shown previously in the study of Ozone on whole fish, and fillets (6).

Ice production was of high quality when raw water was pretreated with Ozone (5ppm). The contrast can be seen in plate # 5. Ice made without Ozone had cell counts in excess of 250. Ozonated ice showed cell counts less than 5. Ice produced in these tests were for the counts supplied, and not for the further treatment or maintenance of the whole fish, or fillets during the tests in July. Use of ozonated ice is not new. Ozone treated raw water sources were first officially noted over 60 years ago in the commercial fish industry in France (7). In that case the shelf life was extended by over 33% with just the use of ozonated ice over fresh fish in the holes of fishing vessels.

Conclusion

Research of the past twenty years has shown that use of Ozone in all facets of meat processing (fish and poultry) could be of great benefit to processor and consumer alike. Technology has progressed over those twenty years, and now Ozone generation is much more proficient, and accordingly more economical to the end user.

Results as summarized in this paper have shown significant potential gains in shelf life, ice quality production, and evidence of more efficient operation of the red water chiller demands in fish processing plants (with implications for the poultry, and seafood industry). These tests have shown that with current technology, Ozone can be applied to those areas reviewed, with impressive results.

Empirical evidence of the data herein offer a multitude of benefits to the industry as a whole. Elimination of chlorine as the prime bactericide is now possible; providing the consumer with a product that has added value, as well as essential health rationale.

Acknowledgements

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Appendix "A"

June Data Set

Location	Cell Cnt.	Coliform	Staph	E. coli
Whole, dressed NT	>5000	+	+	+
Whole, dressed O3	932	+	+	+
Exit Chiller NT	912	+	-	-
Exit Chiller O3	478	+	-	+
Exit Chill Rinse NT	>5000	+	-	+
Exit Chill Rinse O3	912	+	-	+
Fillet NT	>5000	+	-	-
Fillet O3	468	+	-	-
Whole, dressed (belt) NT	>5000	+	-	+
Whole, dressed (belt) O3	750	+	-	+

July Data Set

Location	Cell Cnt.	Coliform	Staph	E. coli
Exit Chiller (whole) CT	2000	4	-	<3
Exit Chiller (whole) CT	1400	<3	-	<3
Exit Chiller (whole) O3	80	<3	-	<3
Exit Chiller (whole) O3	40	<3	-	<3
Fillet Belt NT	85,000	640	-	4
Fillet Belt NT	17,000	93	-	<3
Fillet Belt NT	7,500	9	-	<3
Fillet O3	120	<3	-	<3
Fillet O3	130	<3	-	<3
Fillet O3	190	<3	-	<3
Ice w/o Treatment	230	<3	-	<3
Ice w/o Treatment	390	<3	-	<3
Ice w/O3	1	<3	-	<3
Ice w/O3	2	<3	-	<3

Notes:
    Table definitions are: Cell Cnt., cell count by swab method (4 sq.in. area swabed on each sample); NT, no treatment; CT, chlorine treatment; O3, Ozone treatment; multiple tests in each category were made, this is a summary of those tests
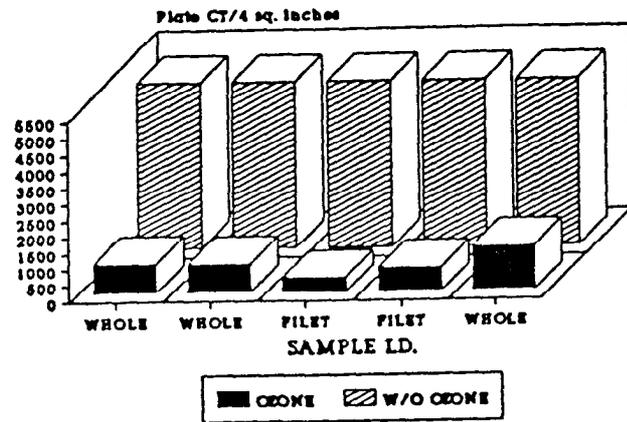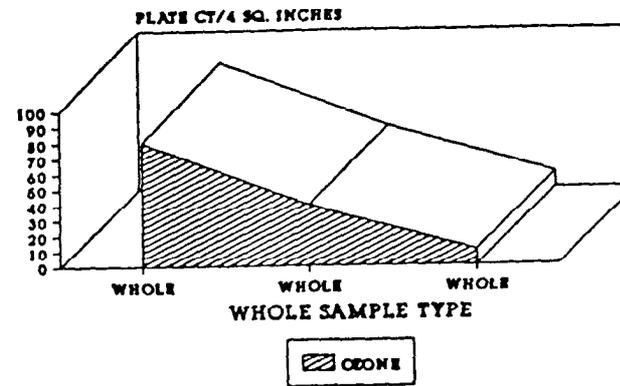
JUNE ON-SITE TESTS

Plate CT/4 sq. inches

6500
6000
4500
4000
3500
3000
2500
2000
1500
1000
500

WHOLE   WHOLE   FILET   FILET   WHOLE
SAMPLE I.D.

■ OZONE   ▨ W/O OZONE

PLATE #1

JULY ON-SITE TESTS
CHILLER TESTS

PLATE CT/4 SQ. INCHES

100
90
80
70
60
50
40
30
20
10

WHOLE   WHOLE   WHOLE
WHOLE SAMPLE TYPE

▨ OZONE

PLATE #2

JULY ON-SITE TESTS
CHILLER TESTS

PLATE CT/4 SQ. INCHES

2000
1750
1500
1250
1000
750
500
250
0

WHOLE CT   WHOLE CT   WHOLE CT
WHOLE SAMPLE TYPE

▦ WITHOUT OZONE
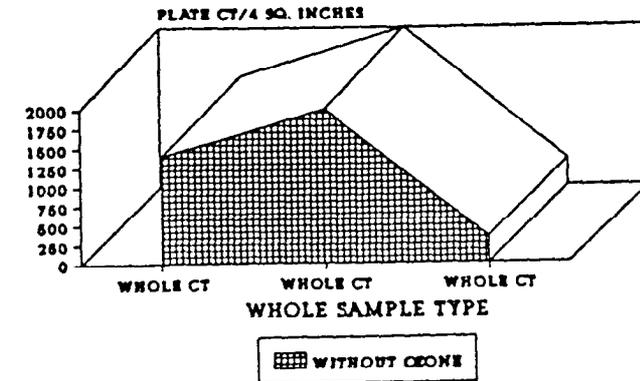
PLATE #3

FILET NON TREATED

PLATE COUNT/4 SQ. INCHES

80
70
60
50
40
30
20
10
0

FILET W/O TREATMENT   FILET W/O TREATMENT   FILET W/O TREATMENT

▨ UNTREATED FILET

PLATE #4

SHELF LIFE

DAYS

16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

▦ KARASUCHI   ▨ STANDARD TREATMENT   ▩ OZONE TREATMENT
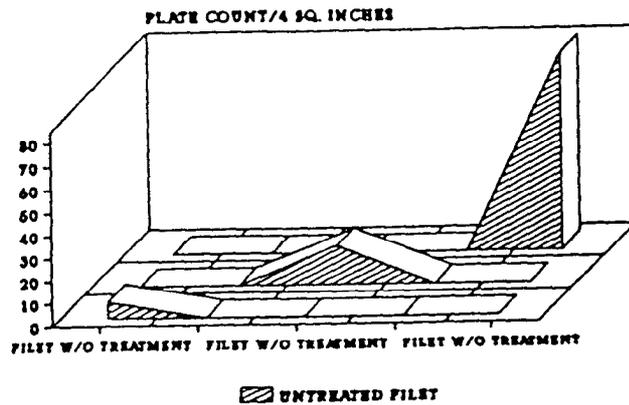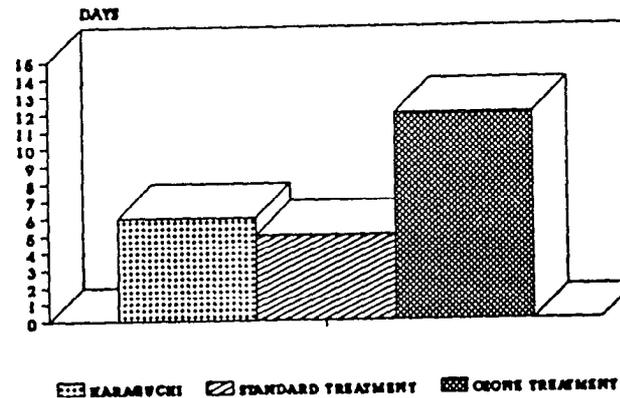
ICE PRODUCTION
NON TREATED VS OZONE

PLATE CT/PER SAMPLE   PLATE CT/PER SAMPLE

300

200

100

0

SAMPLES

▦ NON TREATED   ▨ OZONE TREATED

PLATE #6