

AN EXAMINATION OF THE RELATIVE IMPACT OF COMMON POTABLE WATER DISINFECTANTS (CHLORINE, CHLORAMINES AND CHLORINE DIOXIDE) ON PLASTIC PIPING SYSTEM COMPONENTS

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ABSTRACT

Disinfectants are commonly added to potable water to control bacteria, viruses, protozoa, algae and fungi which can potentially lead to waterborne diseases. The three most common disinfectants used for maintaining a disinfectant residual in North America are chlorine, chloramines and chlorine dioxide. While these disinfectants are all oxidants, their unique characteristics can result in a significantly different impact on the performance of different plumbing system components. In this paper, the chemistry and characteristics of the different oxidants is discussed in the context of oxidative degradation of plumbing system components.

INTRODUCTION

Plastic piping materials have enjoyed a long and successful history. Since the introduction of the first commercial thermoplastic pipe in the 1940's, plastic pipe usage and applications have continued to expand. In the last 25 to 30 years, plastic piping products have become the predominant piping materials in many markets. As a result of the high demand, the availability and types of plastic piping products have increased significantly (1).

One area of rapid growth for plastic piping products is in the area of hot and cold potable water transport. Due to the durability, resistance to corrosion, installation advantages and overall cost benefits, plastic piping materials have quickly become the material of choice in this market. The acceptance of plastic piping materials has also been facilitated by the proactive approach of the industry in the development of standards to ensure product performance in the application. One area of significant research has been in the development of methodologies to ensure resistance of plastic piping materials to the disinfectants commonly added to potable water to maintain the integrity of the water through the distribution system to end use by the consumer. This paper examines the oxidation mechanisms of plastic piping materials observed in testing to these methodologies for the three common potable water disinfectants: chlorine, chloramines and chlorine dioxide.

POTABLE WATER AND THE CHEMISTRY OF DISINFECTANTS

Potable water is commonly treated with disinfectants to make it suitable for drinking. Based on the AWWA *Water Stats* (2), the primary disinfectants added in post-disinfection treatment in the United States are chlorine, chloramines and chlorine dioxide. Chlorine is observed to be the most popular disinfectant followed by chloramines. These disinfectants are relatively strong oxidizers and, even at the relatively low levels used in potable water treatment, have been reported to impact the long-term performance of materials used in potable water (3, 4). While these disinfectants are all oxidants, their unique characteristics can result in a significantly different impact on the lifetime of materials used in potable water applications.

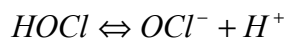
Table I provides a summary of the maximum residual disinfectant level of the different disinfectants as listed in the EPA *Alternative Disinfectants and Oxidants Guidance Manual* (5).

Table I: Summary of the Maximum Concentration Limits

| Disinfectant | Maximum Residual Disinfectant Level (ppm) |
|------------------|---|
| Chlorine | 4 (as Free Cl ₂) |
| Chloramines | 4 (as Total Cl ₂) |
| Chlorine Dioxide | 0.8 (as ClO ₂) |

CHLORINE

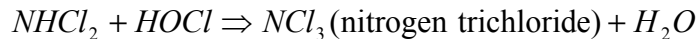
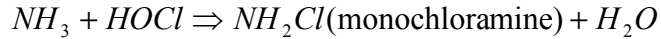
Chlorine (Cl₂) is added for disinfection in the form of chlorine gas or a hypochlorite. Chlorine gas dissolves in water. The resulting solutions form an equilibrium between chlorine, hypochlorous acid (HOCl) and the hypochlorite ion (OCl⁻) as shown below:



Within the pH range typically observed in potable water applications, the chlorine dissociation reaction is essentially driven to completion to produce hypochlorous acid (HOCl). The hypochlorous acid is the primary disinfecting agent. The hypochlorous dissociation equilibrium is dependent on the pH of the water, with higher pH leading to greater dissociation of the hypochlorous acid and higher levels of the less reactive hypochlorite ion (OCl⁻). The aggressiveness of chlorinated potable water is, therefore, a function of both the overall chlorine concentration and the pH of the water. This pH dependency and its impact on performance of plastic piping materials in potable water applications has been described elsewhere (6). The maximum EPA residual chlorine level is 4 ppm with actual usage levels typically much lower.

CHLORAMINES

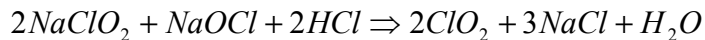
Chlorine, in the form of hypochlorous acid, and ammonia are used to produce chloramines (CLA). There are three types of chloramines:



The fraction of each type of chloramines present is dependent on the chlorine to ammonia ratio as well as the pH. Due to taste and odor issues with dichloramine and nitrogen trichloride, monochloramine is typically the prominent species present for chloramines disinfection (5). The maximum EPA residual chlorine level is 4 ppm with actual usage levels typically much lower.

CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) differs from chlorine and chloramines in that it disinfects by oxidation and it does not chlorinate (5). Chlorine dioxide may be produced many different ways. One method using sodium chlorite ($NaClO_2$) and sodium hypochlorite ($NaOCl$) is shown below:



Chlorine Dioxide remains a gas dissolved in the water. The maximum EPA residual chlorine level is 0.8 ppm with actual usage levels typically much lower.

The plastic piping industry has been proactive in the development of validation methodologies to ensure the long-term performance of plastic piping materials in potable water applications. This has resulted in the development of several different methodologies.

One test method, ASTM D6284, involves boiling pipe specimens in a flask with chlorine and chloramines. This method provides an indication of the relative resistance of the materials under the test conditions by measuring changes in weight, volume and hardness. It does not, however, provide any specific performance projections under end-use conditions. The methodology has been primarily applied to elastomeric materials.

Three test methods for chlorine resistance testing, ASTM F2023, ASTM F2263 and NSF P71 Protocol have been developed to examine the chlorine resistance of plastic piping materials in potable water applications. These test methods involve testing of plastic piping materials under accelerated conditions (elevated temperature) with extrapolation back to end-use temperatures to provide a benchmark for performance. Specimens are tested in the form of pipe in a pressurized system with a continuous flow of water. The water quality is controlled to maintain a residual disinfectant level that is aggressive yet reflective of the worst case water quality conditions that would be observed in service. Elevated temperatures are used to accelerate and generate failures within a reasonable timeframe. Testing is conducted at multiple temperatures and pressures and fitted with the Rate Process Model to enable extrapolation to end-use conditions. These three methodologies were developed with

chlorine treated water as the test fluid. This was done as chlorine is by far the most prevalent disinfectant, is typically observed to be more oxidatively aggressive toward thermoplastic piping materials than chloramines and is typically used at much higher levels than chlorine dioxide, being therefore, directional for any oxidant. There has, however, been recent interest in applying these methodologies to chloramines and chlorine dioxide treated water. As part of a larger research program examining the application of these methodologies to chloramines and chlorine dioxide, this paper examines the mechanisms of oxidation observed for the three different oxidants in accelerated testing.

EXPERIMENTAL

A standard commercial ½" SDR-9 PEX tubing meeting the dimensional requirements of the ASTM F876 standard (7) was used for all testing. Disinfectant resistance testing was conducted in general conformance with the ASTM F2023 method with the exception of water quality for the chlorine dioxide and chloramines testing (8). Water qualities were controlled to obtain a pH of 6.8 and concentration of 4.3 ppm for all three disinfectants (chlorine, chloramines and chlorine dioxide). Fresh Reverse Osmosis water, prepared to the required water quality, is continuously passed through the specimens. Test specimens were internally exposed to continuously flowing test water at two elevated temperatures and constant internal pressure. All of the specimens were tested with ASTM F1807 (9) brass insert fittings. Failure was defined as a loss of fluid through the wall of the pipe.

After testing, the following test methods were performed on the selected tested specimens: Visual examination of the specimens was performed to identify the modes of failure, Oxidation induction time (OIT) was performed in general accordance with ISO 11357-6-2002 (E) at 200 °C. Specimens were taken from the inner and outer surfaces as well as from the bulk pipe wall and Micro-attenuated total reflection Fourier Transform Infrared Spectroscopy (micro-ATR) was performed. The inner surface and the fracture surface were examined. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray analysis (EDX) was performed on the inner surface and the fracture surface.

RESULTS AND DISCUSSION

VISUAL EXAMINATION OF THE FAILURES

The failure specimens resulting from all three disinfectants appear to have similar failure characteristics. The inner surface of the pipe specimens exhibited a layer of highly degraded and discolored material. Micro-cracking of the inner surface is also visible. Around the point of failure, the micro-cracks appear to have coalesced into large cracks in the axial direction parallel to the axis of the specimen. Sectioning of the wall reveals that the micro-cracks have propagated radially beyond the highly degraded layer into the bulk of the wall forming fissures. The surfaces of the fissures show signs of oxidation. The area localized around the failure point exhibits many deep cracks and typically one or more fissures that have visibly expanded. Failure is observed as a single fissure penetrating through the wall leading to a brittle slit or pinhole and to the loss of test fluid. The point of failure was

typically near the inlet fitting (area of highest flow turbulence). The failures for all three oxidants appear to be typical of Stage III brittle oxidative failures.

CHLORINE DIOXIDE EXPOSED SPECIMENS

Figure I shows the inner surface degradation and cracking observed by SEM for the chlorine dioxide tested specimen. In Figure II, a cross-section of the failure crack is shown. Cracking and degradation, consistent with brittle oxidation, is observed through the pipe wall. The degradation level is observed to be highest at the inner exposed pipe surface and decreases through the pipe wall. Rupture of the final section of the wall appears to have occurred through a ductile or fast fracture type of mechanism and does not show the characteristics of degradation observed in the inner and mid pipe wall. Oxygen (as observed by EDX (Table II)) is present through the specimen wall, indicating oxidation of the specimen through the fracture surface. EDX analysis also reveals trace levels of chlorine near the inner surface. The presence of the carbonyl peak, as shown in the FTIR spectrum in Figure III in the region of 1812 to 1660 cm^{-1} , provides further evidence of oxidation of the inner pipe surface. A significant overall depletion in the stabilizer, as indicated by the significant decrease in the OIT values in Table II, is also observed through the entire specimen. Overall, oxidative degradation are highest at the inner exposed surface decreasing through the pipe wall.

Figure I: SEM Image of the Chlorine Dioxide Exposed Specimen, Inner Surface

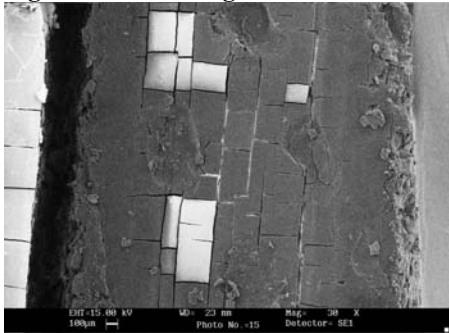


Figure II: SEM image of the fracture face at the crack

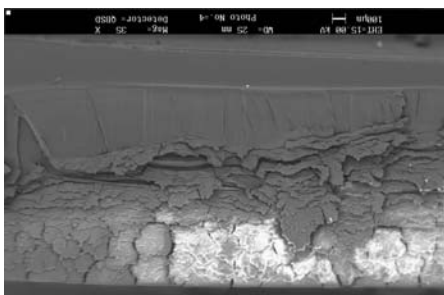
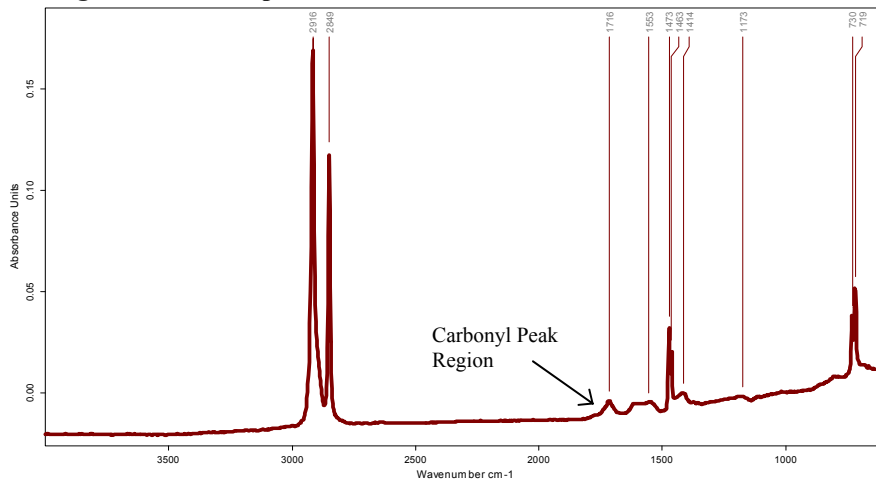


Table II: OIT of the Chlorine Dioxide sample

| | Location | OIT (min) | EDX Semi-Quantitative Results (wt%) | | |
|-------------------|---------------|-----------|-------------------------------------|--------|--------------|
| | | | Carbon | Oxygen | Chlorine |
| Tested specimen | Inner Surface | 0.29 | 80 | 16 | 0.3 |
| | Mid Wall | 5.6 | 84 | 16 | Not Detected |
| | Outer Surface | 3.1 | 85 | 14 | Not Detected |
| Untested specimen | Mid Wall | 127 | - | - | - |

Figure III: FTIR spectrum of the inner surface near the crack for a Chlorine Dioxide exposed sample



Similar analysis of samples exposed for different exposure periods shorter than ultimate failure suggests that the overall failure mechanism is: depletion of stabilizers at the inner pipe surface, oxidation of the inner layer, micro-cracking of the inner layer, crack propagation through the wall with oxidation in advance of the crack front and final rupture of the remaining ligament thickness resulting in ultimate failure.

CHLORAMINES EXPOSED SPECIMENS

Extensive degradation and flaking of the inner surface of the chloramines exposed specimen is observed in the SEM of Figure IV. Similar to the chlorine dioxide exposed specimen, the cross-section of the failure crack, as shown in Figure V, is observed to have cracking and degradation consistent with brittle oxidation. The observed degradation is heaviest at the inner pipe surface and decreases through the specimen. Rupture of the final section of the wall appears to have occurred through a ductile or fast fracture type of mechanism and does not show the characteristics of degradation observed in the inner and mid pipe wall. EDX reveals oxygen through the specimen wall with only a trace level of chlorine in the mid wall. Oxidation, as observed by the presence of carbonyl peaks in Figure VI, is observed to be present from the inner to the mid pipe wall. No significant degradation is observed near the outer wall (confirming rupture of the final ligament thickness through non-oxidative mechanisms). Significant depletion of the stabilizer, as observed by the low OIT values in Table III, is observed through the entire pipe wall.

Fig IV: SEM image from inner surface of Chloramines sample

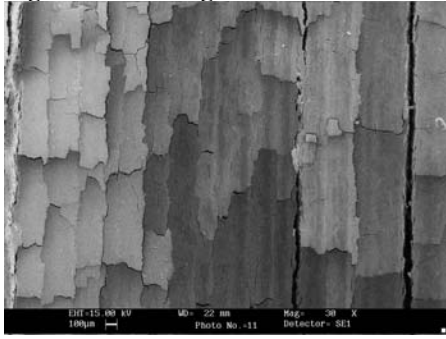


Fig V: SEM image of the fracture face at the crack of Chloramines sample

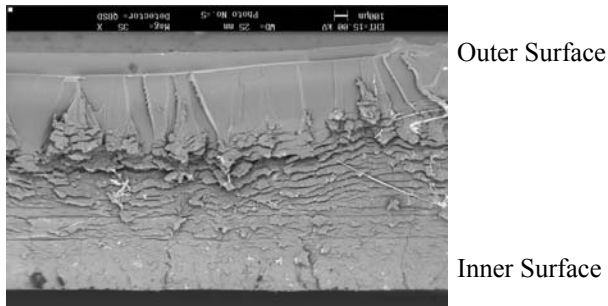
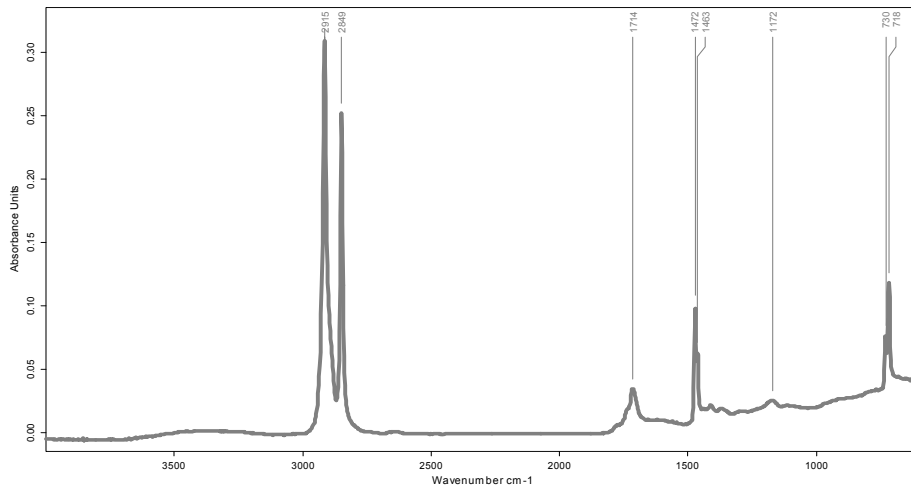


Table III: OIT of the chloramines sample

| | Location | OIT (min) | EDX Semi-Quantitative Results (wt%) | | |
|-------------------|---------------|-----------|-------------------------------------|--------|--------------|
| | | | Carbon | Oxygen | Chlorine |
| Tested specimen | Inner Surface | 0.13 | 81 | 19 | Not Detected |
| | Mid Wall | 0.73 | 80 | 19 | 0.3 |
| | Outer Surface | 0.95 | 85 | 15 | Not Detected |
| Untested specimen | Mid Wall | 127 | - | - | - |

Fig VI: FTIR spectrum of the inner surface near the crack of the chloramines sample



Similar analysis of samples exposed for different exposure periods shorter than ultimate failure suggests that the overall failure mechanism is: depletion of stabilizers at the inner pipe surface, oxidation of the inner layer, micro-cracking of the inner layer, crack propagation through the wall with oxidation in advance of the crack front and final rupture of the remaining ligament thickness resulting in ultimate failure.

CHLORINE EXPOSED SPECIMENS

As shown in Figure VII, extensive micro-cracking of the inner surface is observed for the chlorine exposed specimen. The fracture surface (Figure VIII) shows cracking and degradation consistent with oxidative degradation. EDX analysis reveals that Oxygen is present through the entire specimen wall. Chlorine is observed in the inner and mid walls (Table IV), consistent with chlorine substitution on the PEX backbone. The levels observed are noticeably higher than the trace levels observed for the chlorine dioxide and chloramines tested specimens. Oxidation is observed through the entire specimen wall thickness, with a lower level of oxidation near the outer surface, as indicated by the presence of the carbonyl peaks shown in Figure IX. The OIT values in Table IV indicate significant stabilizer depletion through the entire specimen wall thickness.

Fig VII: SEM image from inner surface of Chlorine sample

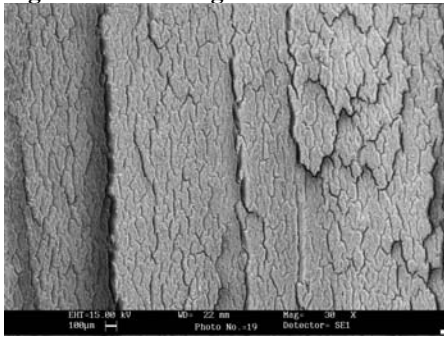


Fig VIII: SEM image from inner surface of Chlorine sample

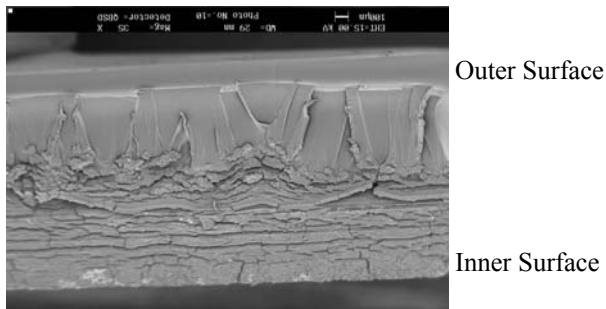
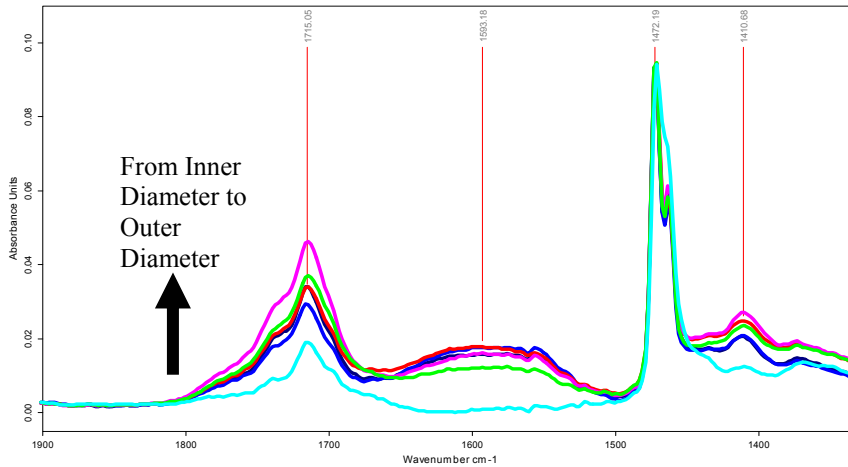


Table IV: OIT of the Chlorine sample

| | Location | OIT (min) | EDX Semi-Quantitative Results (wt%) | | |
|-------------------|---------------|-----------|-------------------------------------|--------|--------------|
| | | | Carbon | Oxygen | Chlorine |
| Tested specimen | Inner Surface | 0.23 | 78 | 17 | 2.0 |
| | Mid Wall | 0.91 | 80 | 18 | 1.4 |
| | Outer Surface | 0.86 | 83 | 16 | Not Detected |
| Untested specimen | Mid Wall | 127 | - | - | - |

Fig IX: FTIR spectrum of the Chlorine sample



Similar analysis of samples exposed for different exposure periods shorter than ultimate failure suggests that the overall failure mechanism is: depletion of stabilizers at the inner pipe surface, oxidation of the inner layer, micro-cracking of the inner layer, crack propagation through the wall with oxidation in advance of the crack front and final rupture of the remaining ligament thickness resulting in ultimate failure.

A COMPARISON BETWEEN DISINFECTANTS

Based on the analysis conducted, the microscopic oxidation and degradation mechanisms observed for the three different disinfectants look similar. Degradation and cracking are observed on the inner surface and cracking consistent with brittle oxidation is observed through the majority of the specimen wall. The portion near the outer wall of the failure points are observed to exhibit little oxidation and appear to be more consistent with a fast ductile failure which may have occurred once the wall thickness was too thin to withstand the internal test pressure. Both the presence of oxygen observed in EDX analysis and the presence of carbonyl peaks in the FTIR analysis provide clear evidence that oxidation has occurred. Significant depletion of the stabilizer is observed in all three disinfectants as observed by the OIT values.

The consistency observed in the failure mechanism for the different oxidants suggests that the methodologies developed for chlorine resistance testing can also be applied to analysis of the impact of chloramines and chlorine dioxide on pipe performance.

While the macroscopic mechanisms observed appear similar between the different oxidants, the overall aggressiveness of the oxidants at the test conditions is observed to vary noticeably. Relative test lifetimes for the three different oxidants at the test conditions vary by a factor of three. While some of this difference can be explained based on the relative oxidative aggressiveness of the different oxidants the relative test lifetimes suggest that other more subtle mechanisms may be at play. Additional research is underway to further characterize the specific mechanisms for the different oxidants and confirm the applicability

of the standard test methodologies in assessing resistance to chloramines and chlorine dioxide.

CONCLUSIONS

Based on the analysis conducted, the microscopic oxidation and degradation mechanisms observed for the three different disinfectants look similar. The consistency observed in the failure mechanism for the different oxidants suggests that the methodologies developed for chlorine resistance testing can also be applied to analysis of the impact of chloramines and chlorine dioxide on pipe performance. While the macroscopic mechanisms observed appear similar between the different oxidants, the overall aggressiveness of the oxidants at the test conditions is observed to vary noticeably. Additional research is underway to further characterize the specific mechanisms for the different oxidants and confirm the applicability of the standard test methodologies in assessing resistance to chloramines and chlorine dioxide.

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