ASSESSING MATERIAL PERFORMANCE IN CHLORINATED POTABLE WATER APPLICATIONS

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ABSTRACT

The chlorine present in potable water as a disinfectant has been reported to reduce the lifetime of some plumbing system components. In this study the nature of the failure mechanism of a commercial cross-linked polyethylene (PEX) pipe material exposed in the laboratory to chlorinated potable water is examined. The observed failure mechanism for laboratory tested PEX pipe materials is seen to be similar to the failure mechanism observed for field failures of polybutylene (PB) pipe materials, indicating that laboratory testing can replicate potential failure mechanisms in service. Water quality, or more specifically, chlorine level, is seen to have a significant impact on material performance. Test lifetimes are seen to be noticeably lower for chlorinated potable water, even at chlorine levels as low as 0.1 mg/L (ppm), than for non-chlorinated water. Through accelerated testing at multiple temperature and pressure conditions and the use of the Rate Process Model, a model to estimate the test lifetime of the PEX pipe material at end use conditions is developed. Based on this analysis the PEX pipe material examined in this study appears to have good resistance to chlorinated potable water. The extension of this testing methodology to other materials and water qualities is discussed.

INTRODUCTION

Potable water in North America is commonly treated to make it suitable for drinking. Part of this process is the addition of disinfectants such that a disinfectant residual is maintained through the distribution system to protect the treated water. The most common disinfectants used in this process are chlorine and chloramines. In the United States, it is reported[1] that approximately 68% of utilities add chlorine and 8% use chloramines to maintain disinfectant residuals in treated surface water. These percentages, especially for chloramine usage, are even higher among the larger utilities that serve the bulk of the US population.

Both chlorine and chloramines are relatively strong oxidizers and, even at the relatively low levels used in potable water treatment, have been reported to impact the lifetime of materials used in potable water applications.[2,3] The early failure of polybutylene (PB) piping systems has been attributed to accelerated degradation due to chlorine in potable water.[3,4] Failures of both the PB piping and the acetal fittings used in these systems have

been reported.[3,10] Chloramines and chlorine have been reported to degrade elastomers used in potable water applications.[2]

When chlorine is added to water the following equilibrium reactions occur[1]:

$Cl_2 + H_2O \quad HOCl + H^+ + Cl^-$ (1).

$HOCl \quad OCl^- + H^+$ (2).

The equilibrium in (1) is driven essentially to complete conversion of chlorine to hypochlorous acid (HOCl) at typical potable water conditions. The hypochlorous acid can further dissociate to form the hypochlorite ion (OCl^-), a reaction which is pH dependant and whose equilibrium shifts considerably over the pH range typically found in potable water applications (6.5 – 8.5). At a pH of 6.5, chlorine exists almost completely as HOCl. At a pH of 8.5, approximately 90% of the HOCl is converted to the OCl^-. The HOCl, considered to be a much more potent oxidizer than the OCl^-,[11] is believed to be the primary species responsible for chlorine induced oxidative degradation. The oxidizing aggressiveness of chlorinated potable water varies widely with pH. Testing is generally conducted at lower pH values so that the chlorine is largely present as HOCl and the water, therefore, is in a more aggressive state in terms of oxidation. In this paper the term 'chlorine' will be used to refer to the free chlorine present in the water as either HOCl or the OCl^-.

The change in oxidative ability of chlorinated water due to the shifting chlorine equilibrium can be captured through the use of the Oxidation Reduction Potential (ORP).[5] ORP is a measure of a solution's ability to oxidize and captures all oxidizers present in the water (i.e. is not specific to chlorine). A higher ORP reading is generally indicative of water that will be more aggressive oxidatively. For reference, deionized water has an ORP in the range of 200 – 300 mV, while the recommended minimum level for maintaining swimming pool sanitation is 750 mV. Deionized water with 0.5 mg/L (ppm) chlorine has an ORP of approximately 600 mV at a pH of 8.5 and 820 mV at a pH of 6.5. ASTM Standard F2023: 'Test Method for Evaluating the oxidative Resistance of Cross-linked Polyethylene (PEX) Tubing and Systems to Hot Chlorinated Water' specifies testing with a minimum ORP of 825 mV. A detailed analysis of water quality and the impact it has on material performance is discussed in detail elsewhere.[6]

Several methodologies for assessing a material's resistance to chlorine (or chloramines) have been proposed.[2,7,8,9] ASTM Standard D6284 provides a test method for evaluating the ability of rubber materials to withstand the effects of aqueous chlorine and chloramine solutions.[7] Testing is conducted at slightly elevated temperatures (recommended 70^{o}C) in aqueous solutions with relatively high levels of total chlorine (50 mg/L (ppm)). Samples are immersed in aqueous chlorine or chloramine solutions at the test temperature with the test solutions being changed daily. Material properties are measured before and after exposure. The procedure provides a relative indication of a material's susceptibility to chlorine or chloramines but does not provide a means of estimating a performance lifetime in the field. Both ASTM F2023[9] and the NSF Protocol

for Chlorine Resistance of Plastic Piping Materials[8], involve testing of end use product under pressure in a flowing system. The continuous flow of water ensures that a constant and controlled level of chlorine is present in the test water throughout testing. Samples are tested under aggressive water quality conditions that are intended to represent the potential worst case water quality that might be seen in service. Elevated temperatures are used to accelerate failures. Testing is conducted at multiple temperatures and pressures. Multiple linear regression is then used to fit the experimental data to the Rate Process Model to allow determination of an extrapolated test lifetime under end use conditions.

In this work, the effects of the residual chlorine in potable water on a commercially purchased polyolefin piping material (cross-linked polyethylene (PEX)) are examined. The mechanism of degradation and ultimate failure of laboratory exposed samples is analyzed. The nature of the observed laboratory failures for the PEX material are compared with field failures of a PB piping material. The impact of chlorinated versus non-chlorinated water on material lifetime is examined. Accelerated testing at multiple temperatures and pressures and application of the Rate Process Model is used to develop an extrapolated test lifetime under end use conditions. This approach is shown to provide a method for assessing material performance in potable water applications that can be readily extended to other materials or water qualities. It also demonstrates that, for the particular PEX piping material studied, very good field performance is predicted.

EXPERIMENTAL

The PEX piping material studied was a commercially purchased PEX pipe material. The pipe was a nominal ½" diameter and was manufactured in accordance with ASTM F876/F877 and CSA B137.5 and certified for use in potable water applications by NSF and CSA. The pipe was tested in 15" lengths with commercially purchased copper insert fittings manufactured according to ASTM F1807.

Testing was conducted in general accordance with ASTM F2023[9] and the NSF Protocol.[8] Pipe samples were exposed to continuous flowing water of controlled quality while under constant internal pressure. Failure, defined as any loss of fluid through the wall of the pipe, was sensed by computer monitored humidity sensors. Select samples were removed prior to failure to examine the progression of the failure process. Temperature, pressure, chlorine level and pH were continuously monitored and controlled. ORP was measured for reference. Unless otherwise stated, testing was conducted with a nominal water quality of pH=6.8, chlorine level =4.3 mg/L and ORP=860 mV.

The exposed pipe surfaces and fracture surfaces were analyzed using a Stereo Optical Microscope with a computerized Image Analyzer. Samples were prepared by cutting with a fresh razor blade.

FTIR samples were microtoned from the pipe wall.

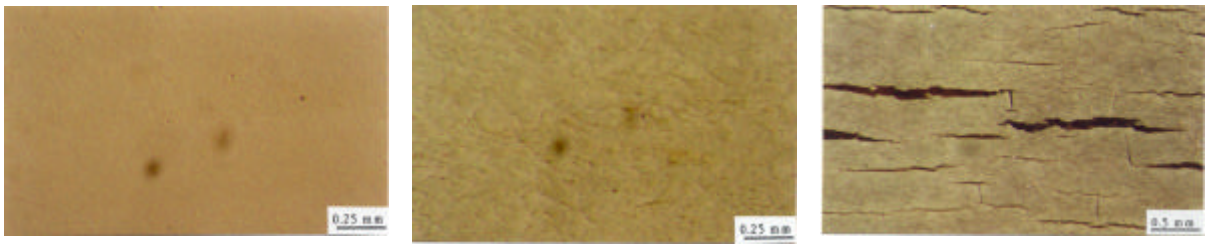
RESULTS AND DISCUSSION

Nature of Failure Mechanism

Samples were generally tested to failure, with failure being defined as any leak or loss of fluid through the pipe wall. For select conditions, samples were also removed at various times prior to ultimate failure in order to examine the progression of the failure process.

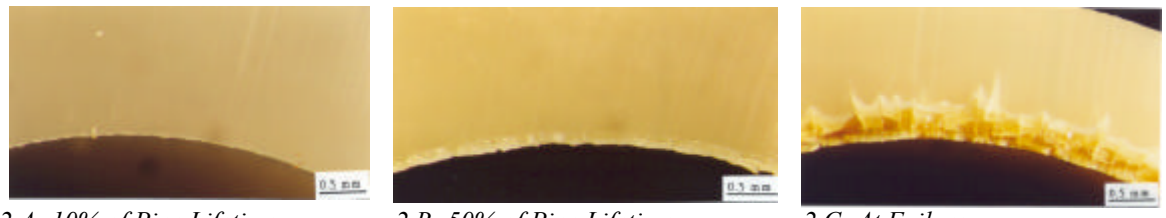
Figure 1 shows the inner exposed surface of the PEX piping material as a function of exposure time. Figure 2 shows the same samples looking through the wall of the exposed pipe specimens (with the inner exposed surface facing the bottom of each picture). At 10% of the lifetime a fine a fine degradation layer has formed on the inner exposed surface as seen in Figures 1A and 2A. At 50% of the lifetime, micro-cracks are visible on the inner exposed surface (Figure 1B). The degradation layer thickness has increased (Figure 2B) and the micro-cracks are starting to propagate radially through the pipe wall. At ultimate failure several very large micro-cracks are visible on the inner exposed surface (Figure 1C) and the degradation layer thickness has increased significantly (Figure 2C). Ultimate failure occurred when one of the micro-cracks propagated through the entire wall thickness resulting in a brittle slit failure approximately 2 mm in length.

Figure 1: Progression of Chlorine Induced Degradation of a PEX Pipe Material: Inner Pipe Surface



1.A: 10% of Pipe Lifetime *1.B: 50% of Pipe Lifetime* *1.C: At Failure*

Figure 2: Progression of Chlorine Induced Degradation of a PEX Pipe Material: Through the Pipe Wall.



2.A: 10% of Pipe Lifetime *2.B: 50% of Pipe Lifetime* *2.C: At Failure*

FTIR analysis of the exposed pipe samples was conducted to examine degradation. Samples were taken from the inner exposed wall, the mid wall and the outer wall for the same pipe samples as Figures 1 and 2. These results and reviewed briefly here and will be discussed in detail in a future paper.[6] Based on the carbonyl peak in the region of 1760 cm^{-1}, it is seen that significant oxidation of the inner exposed pipe surface has occurred at 10% of the test lifetime. No change in oxidation is observed at the mid or outer wall. The chlorine, therefore, appears to have rapidly attacked and oxidized the inner exposed pipe surface. At 50% of the pipe lifetime, increased oxidation is observed at the mid and outer wall. The inner wall still, however, shows a significantly higher level of oxidation. At failure, the mid and outer wall are seen to be further oxidized but still less so than the inner exposed surface.

Figure 3: Radial Crack Growth in a PEX Pipe Material.

Figure 3 shows another view of the propagation of the micro-cracks through the pipe wall. Several large cracks are observed, distributed randomly around the circumference of the pipe. In Figure 4, the axial cross section of the same pipe material is shown. The sample was cut along one of the large longitudinal cracks. The advancing crack front is clearly seen in this view. Regions where multiple small cracks have coalesced to form a larger crack are also visible.

Based on the above observations, the basic mechanism of chlorine attack on PEX materials appears to be:

1. Rapid chlorine oxidation of the inner pipe wall.
2. Once sufficient oxidation and degradation of the inner wall occurs a combination of degradation induced and applied stresses on the inner pipe surface causes micro-cracks to form in the degraded inner layer.
3. The crack density and crack length increase with exposure time. The cracks propagate through the wall of the pipe material.
4. The cracks begin to coalesce to form larger cracks.
5. Ultimately a brittle slit or pin hole failure is observed when a crack propagates through the entire wall thickness.

Other materials have been found to exhibit similar mechanisms of initial chlorine attack with the exact mechanism of ultimate failure being material dependant.

Figure 4: Axial Cross-section of Chlorine Exposed PEX Pipe Material.

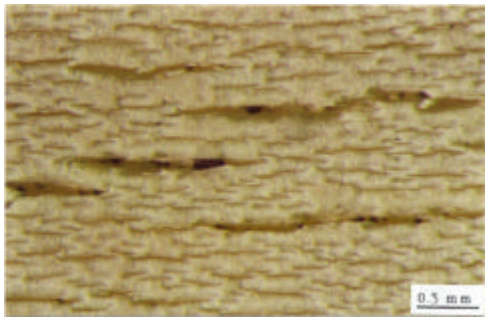
COMPARISION OF OBSERVED FAILURE MECHANISM WITH FIELD FAILURES

In accelerated laboratory testing a key objective of the testing is to replicate the failure mechanism that is observed in the field. For PEX materials there were no field failures available to the authors with which to make comparisons. There have, however, been field failures reported for another polyolefin material, polybutylene (PB).[3] The observed laboratory failures for PEX materials will, therefore, be compared to the observed failure mechanism for PB pipe exposed to chlorinated water.

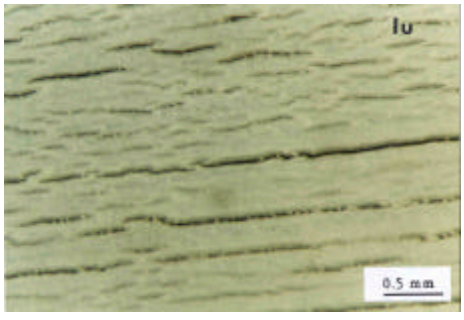
Figure 5 shows the inner exposed pipe surfaces of A: a PEX laboratory failure and B: a PB field failure. The PB field failure was in service for roughly 15 years, exposed to a chlorine level of approximately 1 ppm. Both samples show extensive micro-cracking of the inner exposed surface. The micro-cracks for both materials appear to have coalesced to form larger cracks. Figure 6 shows the same exposed samples looking through the wall. Similar degradation of the inner surface is observed. For both samples the micro-cracks that have initiated on the inner surface are seen to propagate radially through the pipe wall. It is interesting to note what appears to be a higher level of degradation of the PEX material. This may be reflective of the difference in material structure between the PEX and PB materials, or the more aggressive test conditions (higher chlorine level) employed in the laboratory accelerated testing.

The observed failure mechanism for a PEX laboratory failure and a PB field failure appear to be very similar. The accelerated test methodology employed in this study does, therefore, appear able to replicate potential failure mechanisms in service.

Figure 5: Comparison of Observed Failure Mechanism with Field Failures.

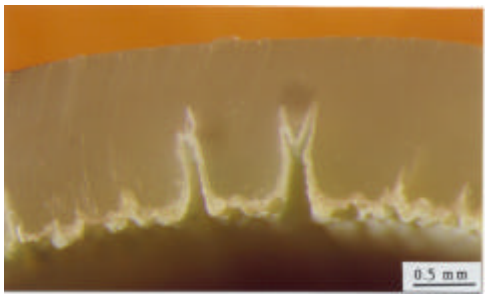


5.A: PEX Laboratory Failure

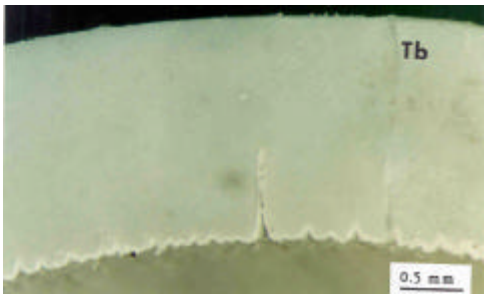


5.B: PB Field Failure

Figure 6: *Comparison of Observed Failure Mechanism with Field Failures.*



6.A: PEX Laboratory Failure



6.B: PB Field Failure

INFLUENCE OF WATER QUALITY ON TEST LIFETIME

In order to examine the impact of water quality (or more specifically chlorine level) on test lifetimes, further testing was conducted with three different water qualities: 1. non-chlorinated water, 2. water with very low residual chlorine (0.1 mg/L (ppm), pH 6.5), and 3. an aggressive water quality (pH 6.8, 4.3 mg/L (ppm) chlorine). For all water qualities, a continuous flow of fresh water through the pipe samples was maintained throughout testing. The test conditions and the relative lifetime of the PEX piping material in the different water qualities is presented in Table 1. Testing was conducted at a single elevated temperature (115 ^{o}C) to accelerate failures.

Comparing the relative test lifetime for the aggressive water quality with that for the non-chlorinated water, the tremendous effects of the chlorinated water on the acceleration of brittle oxidative failure are seen. At this test condition, the non-chlorinated water results in test lifetimes 2.3 times higher than for the chlorinated water. Based on on-going studies, it appears that this difference in performance increases as test temperature is decreased. One would, therefore, predict that at end use temperatures the difference in lifetimes between materials in non-chlorinated versus chlorinated potable water would be very significant. Standard testing methods, which employ stagnant water (where any chlorine, if present, would quickly be consumed to result in non-chlorinated test water) would, therefore, tend to greatly over estimate the oxidative lifetimes in chlorinated potable water environments.

As can be seen based on the relative lifetimes in Table 1, even at chlorine levels as low as 0.1 mg/L (ppm) chlorine, the chlorine can have a significant impact on test lifetimes. Therefore, even though residual chlorine levels may be reduced below initial dosage levels as the water travels through the distribution system and to the home, chlorinated water can still have a potentially significant impact on material lifetimes.

Table 1: Influence of Water Quality of Relative Test Lifetime.

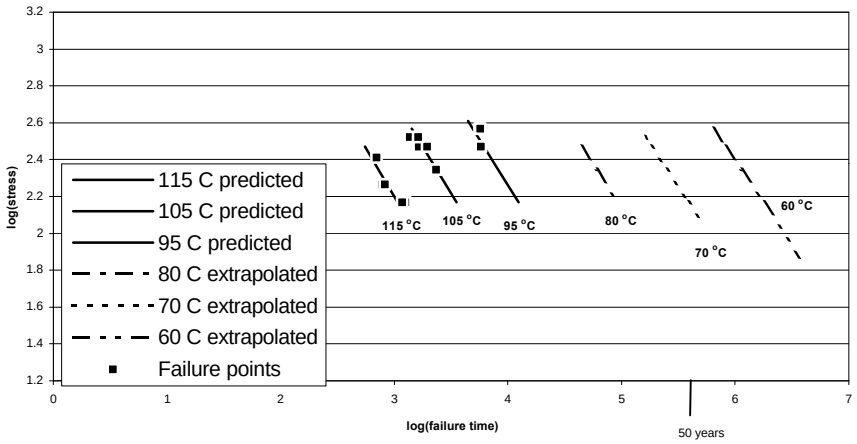
Condition	pH	Free Chlorine (ppm)	ORP (mv)	Relative Lifetime
1	6.8	4	845	1
2	6.5	0.1	715	1.4
3	6.5	0	430	2.3

Given the different relative lifetimes under the three different water qualities studied, it would be expected that plumbing system materials will have a wide range of service lifetimes in application that is dependant on the specific water quality in a given region. Chlorine, therefore, even at relatively low levels is found to significantly reduce pipe lifetime. A more detailed examination of the influence of water quality (studying the impact of chlorine level, pH and ORP) on the performance of materials in potable water applications will be published in detail elsewhere.[6]

PREDICTING PERFORMANCE LIFETIME IN CHLORINATED POTABLE WATER

Given the significant impact of chlorine on a material's brittle oxidative lifetime and reported failures of materials in potable water applications,[3,10] the ability to validate a material's performance prior to field installation is essential. Further, plumbing system materials are often installed in applications requiring service lifetimes of 50 years or more. An accelerated means of assessing field performance is, therefore, required. Current practice[8,9] is to use elevated temperatures to accelerate failure times while testing with a single aggressive water quality to provide a 'worst case' scenario. Testing is conducted at multiple temperatures and pressures and the Rate Process Model is used to model the experimental data. Extrapolation to anticipated end use conditions can then be performed to predict material performance.

Figure 7: Log(Stress) versus Log(Failure Time) for a PEX Pipe Material



This approach was applied to a commercial PEX pipe material, intended for both hot and cold potable water applications. Testing was conducted at eight different temperature and pressure conditions with a total of 16 failure points generated. The test conditions and failure times are presented in Table 2.

The experimental data was fitted to the Rate Process Model:

$$\text{Log (failure time)} = A + B/T + C/T*\log(\text{hoop stress}) \quad (1)$$

using multiple linear regression to solve for the coefficients A, B and C. The resulting equation for predicting failure time as a function of temperature and pressure is:

$$\text{Log (failure time)} = -16.45 + 8367.2/T - 372.2/T*\log(\text{hoop stress}) \quad (2)$$

Figure 7 shows a plot of the experimental failure points and the predicted failure times from the Rate Process Model. From the data it is seen that the Rate Process Model provides a good fit to the experimental data. The R^2 for the regression was 0.98. Also shown in Figure 7 are the extrapolated test lifetimes at lower temperatures.

Table 2: Failure Times for a PEX Pipe Material Exposed to Chlorinated Potable Water.

Run #	Temperature (^oC)	Hoop Stress (psi)	Failure Time (hours)
1	115	259	702
2	115	185	813
3	115	185	784
4	115	185	823
5	115	148	1244
6	115	148	1174
7	105	333	1375
8	105	333	1612
9	105	296	1636
10	105	296	1941
11	105	222	2320
12	105	222	2231
13	95	370	5661
14	95	370	5670 NF
15	95	296	5809
16	95	296	5890 NF

NF = Non-failure, sample still on test

For domestic plumbing applications the commonly accepted most aggressive end use conditions are 80 psi internal pressure and 60 ^{o}C (140 ^{o}F) temperature. In actual application both pressure and temperature, or the combination thereof, would be expected to be below these values. Moreover, most domestic plumbing systems do not experience continuous hot water conditions. These conditions would appear, therefore, to be relatively conservative. The extrapolated test lifetime for the PEX material tested based on these conditions is 93 years with a 95% lower confidence limit of 52 years. This estimate is based on testing at aggressive water quality conditions as well as extrapolation to aggressive end use conditions. Even though the presence of the chlorine in the potable water reduces the anticipated performance lifetime of the PEX pipe material tested, the material still appears to have very good chlorine resistance.

CONCLUSIONS

Chlorine in potable water is seen to accelerate the brittle oxidative failure of a PEX pipe material. The failure mechanism observed in laboratory generated failures for PEX pipe exposed to chlorinated water is consistent with that observed for a field failure of PB pipe. The effects of chlorine on lifetime reduction are observed even at very low levels of chlorine. The Rate Process Model is seen to provide a good fit to experimental data generated by testing to failure at multiple temperatures and pressure conditions. An indication of material performance can then be obtained by extrapolation to end use conditions. Based on this analysis, the PEX pipe material examined appears to have good resistance to chlorinated water.

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