ENVIRONMENTAL FACTORS IN PERFORMANCE FORECASTING OF PLASTIC PIPING MATERIALS

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Abstract

Environmental factors are known to significantly impact the oxidative failure mechanism of materials. For example, the chlorine present in potable water as a disinfectant is an oxidant that has been reported to impact the failure mechanism of materials in potable water applications. In this paper, the relationship between various potable water qualities, with different oxidative potentials, and chlorine induced oxidative failures of plastic piping materials is examined. The primary factors of potable water quality affecting oxidative strength are reviewed. Laboratory exposed pipe samples tested at various water qualities to ultimate failure are examined to determine the impact of water quality on the failure mode. The chlorine in potable water is seen to attack the inner pipe wall causing oxidation and degradation of this inner surface. The stresses on the inner wall lead to micro-crack formation in this degraded layer. These micro-cracks are seen to propagate radially through the pipe wall resulting in a brittle slit type failure. The failure mode is shown to be the same over a range of water qualities. The impact of chlorine is shown to be simply one of oxidation with the rate of degradation primarily related to the oxidative strength of the potable water. For the PEX pipe material examined, it is projected that material performance can significantly exceed the excellent performance predicted based on testing at the aggressive water qualities typically employed in validation testing, depending on the specific water quality of the end use application.

Background

Plastic piping and tubing is commonly used in the transportation and delivery of potable water to industrial, commercial and residential facilities. Environmental factors ultimately determine the lifetime of the pipe in the application. Some of these environmental factors include the installation methods, the operation pressures, the operating temperatures, and the nature of the fluid transported. The impact of many of these factors is well characterized and methodologies have been established to validate performance and provide design rational[1]. The potential chemical impact of the transported fluid on long-term material performance is typically less well characterized. A typical application of plastic piping and tubing in residential and commercial buildings is the use of PEX tubing for conveying of both hot and cold potable water. Potable water, due to the disinfectant residual, has been shown to be a potentially aggressive medium[2]. The PEX industry has been proactive in the development of validation methodologies for ensuring the long-term performance of PEX piping in potable water applications[7,9].

The potable water treatment process typically results in a disinfectant residual to ensure safe water delivery to the consumer. The disinfectant residual used most often in North America is chlorine[3]. Other disinfectants commonly used include chloramines and chlorine dioxide. Chlorinated water, even at low levels, results in a significantly increased oxidative potential of the water. As chlorine has similar oxidative strength to chlorine dioxide, a higher oxidative strength than chloramines and is the most common disinfectant, validation testing for materials in potable water applications is typically focused on chlorine[7,9] (one exception is examination of the impact of chloramines on elastomers[10]).

The characteristics of potable water vary greatly within North America. The EPA guidelines for water entering the distribution system are for a maximum chlorine concentration of 4mg/L and a pH range of 6.5-8.5[3]. The average values for water entering the distribution system are a pH of 7.7 and a chlorine concentration of 1.1 mg/L[4]. The pH of the water is reported to range from 6.1 to 10 and the chlorine is reported as high as 4mg/L. The combination of the pH and the chlorine concentration, along with the other components in potable water, determine the overall oxidative strength of the water. Chlorine in water exists as equilibrium between hypochlorous acid and hypochlorite ions. The equilibrium is very sensitive to pH within the typical range found in potable water. At pH 6.5, the equilibrium is approximately 90% hypochlorous acid and at pH 8.5 only 10% hypochlorous acid. As hypochlorous acid is the much stronger oxidant, the equilibrium is expected to significantly affect the overall oxidative strength of the water. A measure of the overall oxidative strength of water is the oxidation-reduction potential (ORP) measured in mV. The ORP of water generally decreases with increasing pH and increases with increasing chlorine concentration. Given the broad variation in water quality, validation testing is typically conducted at aggressive ‘worst case’ water qualities[7,9].

In this work, the relationship between the potable water quality and the test lifetime of PEX piping is examined. The impact of pH, chlorine concentration, ORP and test temperature on the test lifetime of a PEX tubing material is evaluated using accelerated chlorine resistance testing. Chlorine resistance testing has been demonstrated to be an effective method of evaluating the long-term resistance of materials to oxidative attack[3,5]. A sample of PEX tubing is tested at various water qualities. A design of experiments is used to identify the key parameters and interactions between parameters affecting lifetime. The observed degradation mechanism in different water qualities is examined. It is shown that the degradation mechanism is consistent for the different water qualities and that the ORP of the test water correlates with log(failure time). Based on the projection of the test results to end use conditions, it is predicted that water quality can have a significant impact on material performance. Given that validation testing is typically conducted at very aggressive water quality conditions, for the PEX pipe material examined, these methodologies would appear to provide a conservative means of validating material performance.

Experimental

A standard commercial ½” SDR-9 PEX tubing meeting the dimensional requirements of the ASTM F876 standard[6] was used for all testing. Chlorine resistance testing was conducted in general conformance with the ASTM F2023 method[7]. Test specimens were internally exposed to continuously flowing test water at elevated temperature and constant internal pressure (0.55MPa, 80psig). The outside of the specimens was exposed to stagnant air at the same temperature as the test water. Table 1 summarizes the characteristics of the waters used in testing. The test waters were generated from reverse osmosis (RO) water with the controlled addition of chlorine gas (Cl_2) and the pH adjusted by the controlled addition of sodium hydroxide (NaOH). ORP was measured using a platinum redox electrode. Chlorine, pH and ORP measurements were conducted at room temperature. All specimens were tested with ASTM F1807[8] copper insert fittings. Failure was defined as any loss of fluid through the wall of the pipe. A visual examination of the specimens was conducted following testing to identify the modes of failure.

A full 2^3 factorial design of experiments was conducted to determine the significance of temperature, pH and chlorine concentration on test lifetime. In addition, as shown in Table 1, testing was conducted at a broad range of water qualities to further examine the impact of water quality on oxidative resistance.

Results and Discussion

DOE Analysis

A detailed analysis of the DOE testing is not provided in this paper. The results are, instead, summarized in terms of the key observations.

The overall dataset of the DOE included a total of 32 failure points. The test block is a complete 2^3 DOE with the independent variables of temperature, chlorine level and pH. A DOE analysis was run to determine the significant factors and significant interactions using test time as the dependent variable. The overall regression coefficient (R^2) for the analysis was 0.92. The significant factors were found to be temperature, pH and chlorine level (marginal). As expected, the test lifetimes increased with decreasing temperature, decreasing chlorine concentration and increasing pH. The chlorine level was seen to be only marginally significant which is believed to be more a consequence of the chlorine levels selected, as there is only a small difference in ORP between the levels, rather than a true indication that chlorine is only a marginally significant factor. Testing at a broader range of chlorine levels, as discussed in the next section, confirms this hypothesis.

Impact of Water Quality on Test Lifetime

Table 1 provides a summary of the test lifetimes for testing at a broad range of water qualities. Testing was conducted at two elevated temperatures, 115°C and 105°C. Chlorine levels from 5 to 0.1 mg/L and non-chlorinated water were examined. Testing of some specimens at 105°C was discontinued without failure.

In general, it is observed that there is a broad variation in test lifetime with different water qualities. At the 115°C test conditions, failure times were observed to range from hours to 4589 hours depending on the water quality. Similarly, at 105°C, test lifetimes are seen to range from 2238 hours to greater than 10,160 hours (non-failure). It is notable that, even at chlorine levels of 0.1 mg/L, chlorinated water is significantly more aggressive than non-chlorinated water. For example, at 115°C, the average failure time with 0.1 mg/L chlorine was 1709 hours versus 4589 hours for non-chlorinated water.

Failure Characteristics in Chlorinated Water

Several tests were run with what could be termed ‘high’ chlorine levels. Specimens were tested at 3 and 5 mg/L chlorine and pH 6.5 and 8.5. The test lifetimes ranged from 841 to 4038 hours depending on the test condition. All the failure samples exhibited very similar failure characteristics. The inner surface of the pipe specimens exhibited a layer of highly degraded, discolored material. This layer was brittle and could be readily removed by scraping (which is typical of highly oxidized material). Micro-cracking of the surface is visible in this layer. Around the point of failure, the micro-cracks appear to have coalesced into larger cracks 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. A single fissure penetrating through the wall led to a brittle slit or pinhole failure and to the loss of test fluid. The point of failure was typically near the inlet. Specimens tested in pH 8.5, compared to those tested at pH 6.5, appear to have a glossier appearance and finer micro-cracking with thinner fissures. Fourier Transform Infrared (FTIR) and Oxidation Induction Time (OIT) analysis indicate significant oxidative degradation of the pipe materials.

The specimens tested at 0.1mg/L chlorine and pH 6.5 showed very similar characteristics at test completion to the specimens tested at the higher chlorine levels. Oxidation of the inner layer had occurred with typical micro-cracking of the surface and crack propagation through the wall resulting in brittle slit failures. Again, the samples are observed to be highly oxidized, particularly in the region of the failures.

The observed failure mechanism of the specimens tested in non-chlorinated RO water is generally consistent with the specimens tested with chlorinated water. As with the chlorinated water tested specimens, oxidation, micro-cracking and crack propagation were seen to occur. Similarly, the crack propagation led to a brittle slit failure originating from the inner surface. The failure, however, occurred in a region of localized degradation. Most of the remainder of the specimen did not exhibit the readily apparent extensive degradation as observed in the failure region. The failures appear to be randomly distributed throughout the pipe length, occurring in regions of localized degradation suggesting that degradation begins in a localized region of low oxidative stability. While the generally observed degradation mechanism for specimens tested in non-chlorinated water appears to be consistent with that observed for samples tested in chlorinated water, the observed degradation in chlorinated water appears to be more uniform and less randomized.

Based on the results of this study and previous studies[2,3], the basic mechanism of oxidative degradation of PEX materials appears to be:

- Oxidation of the inner pipe wall.
- Once sufficient oxidation and degradation of the inner wall occurs a combination of degradation induced and applied stresses in the inner pipe surfaces causes micro-cracks to form in the degraded inner layer.
- The crack density and crack length increase with exposure time. The cracks propagate through the wall of the pipe material through a slow crack growth (SCG) process.
- The cracks begin to coalesce to form larger cracks. Degradation continues on the inner layer and may be accompanied by erosion leading to a loss in wall thickness.
- Ultimately a brittle slit or pinhole failure is observed when a crack propagates through the entire wall thickness.

Based on the test results in this study, this same general mechanism appears to be valid irrespective of the water quality. Similar failure mechanisms are seen when testing at different temperatures, low and high pH levels, high and low chlorine levels and with no chlorine. The primary difference in the failures appears to be the greater randomization of the degradation in non-chlorinated water. All the specimen failures are typical of brittle oxidative or Stage III type failures. The similarity of the degradation and failure mechanism in non-chlorinated water and in a broad range of qualities of chlorinated water is indicative that the degradation process is not specific to the chlorine chemistry of the water and is rather more likely due to the overall oxidative effects of the water.

Oxidation Reduction Potential (ORP)

As discussed previously, the Oxidation-Reduction Potential (ORP) is a measure of the overall oxidative strength of the water. In order to examine the relationship between the oxidative strength of the water and test lifetimes, a regression analysis was performed of the test lifetimes over a wide range of water qualities. The ORP values ranged from 430mV for non-chlorinated water to 887mV for the most aggressive condition of 5mg/L chlorine and pH of 6.5. A plot of log (test lifetime) versus ORP for the test data generated at 115°C resulted in a regression coefficient (R^2) of 0.956, indicating a good fit of the data to the regression line. Regression analysis of the log (test time) versus ORP for the 105°C data resulted in an R^2 of 0.952, also indicating a good fit. The data points and regression lines are shown in Figure 1. It is observed, therefore, that there appears to be a good correlation between ORP and log (test lifetime) over a broad range of water qualities, including non-chlorinated water.

It is significant that the relationship between ORP and test lifetime holds over a wide range of chlorine concentrations and a range of pH values. It is also significant that the relationship extends to non-chlorinated water. Both these observations, combined with similarities of the degradation and failure mode over the range of water qualities examined, provide substantial support for the conclusion that the degradation of PEX in chlorinated water is attributable not specifically to the chlorine content or chemistry and rather to the overall oxidative strength of the water.

Based on the test data generated under a range of water qualities, it is possible to make a crude extrapolation of test lifetime to end use conditions for water of various ORP's. Tables 2 & 3 summarize the lifetime predictions at 60°C, a typical end use temperature for hot water piping applications, for a range of ORP's and the pH and chlorine test combinations examined in this paper. While these estimates should be considered very approximate, they do provide insight into the potential impact of water quality on estimated test lifetimes at end use conditions. At both pH 6.5 and 8.5, the difference in the predicted lifetimes between 3 and 5mg/L chlorine is small as shown in Table 3. At both the chlorine levels of 3 and 5mg/L, a shift in pH from 6.5 to 8.5 is predicted to result in approximately a three to four fold increase in test lifetime. Although these numbers are approximate, based on the difference between the relative predicted lifetime in non-chlorinated and 0.1mg/L chlorinated water, it is evident that the addition of only a small amount of chlorine can result in a large change in the predicted lifetime.

In previously reported testing[2], a PEX pipe material examined under very aggressive water quality environments was predicted to have excellent resistance to chlorinated potable water. This testing was conducted at an ORP of approximately 840 mV, in accordance with the ASTM F2023 standard. Based on conservative estimates of end use conditions of continuous 0.55MPa (80 psig) internal pressure and 60°C temperature (In actual application both pressure and temperature, or the combination thereof, would be expected to be below these values) an extrapolated test lifetime of 93 years with a 95% lower confidence limit of 52 years was obtained.

An analysis of the chlorine and pH values reported by water utilities[4] for water entering the distribution system predicts average ORP values of around 750 mV with values extending to the low 800s. As the chlorine levels, and hence ORP values, are predicted to decline through the distribution system and through the home, the standard test conditions would appear to represent conservative worst case water qualities. Given the relative predicted test lifetimes at 60°C (Table 2), it is seen that the performance of the PEX pipe material, projected based on testing at approximately 840 mV, should provide a conservative validation of performance over the broad range of potential water qualities in service.

Conclusions

The failure mode in non-chlorinated potable water of a PEX pipe appears to be similar to that observed in the presence of chlorinated potable water at the tested conditions. ORP has been shown to correlate well with failure times at the two tested temperatures. These findings are suggestive that the degradation and failure of PEX in chlorine resistance testing is largely a phenomenon of the overall oxidative strength of the solution and not due to specific chlorine chemistry. For the PEX pipe material examined, it is projected that material performance can significantly exceed the excellent performance predicted based on testing at the aggressive water qualities typically employed in validation testing, depending on the specific water quality of the end use application.

References

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Table 1: Summary of Failure Times and Test conditions for DOE (Temperature, Chlorine, pH)

Condition Number	Temperature (°C)	Chlorine Level (mg/L)	pH	ORP (mV)	Average Failure Time (hours)
1	115	5	6.5	887	841
2	115	3	6.5	873	1097
3	115	0.1	6.5	715	1661
4	115	0.1	6.5	715	1757
5	115	0	6.5	430	4589
6	105	5	6.5	887	2238
7	105	3	6.5	873	2311
8	105	5	8.5	778	3416
9	105	3	8.5	758	4038
10	105	0.1	6.5	715	5667
11	105	0.1	6.5	715	5761 Non Failure
12	105	0	6.5	430	10160 Non Failure

Table 2: Relative Expected Test Lifetime at 60°C for a range of ORP's

ORP (mV)	840	825	800	775	750	500
Estimated Relative Lifetime	1	1.2	1.6	2.2	2.9	57

Table 3: Estimated Test Lifetimes at 60°C as a Function of Test Water Quality

pH	Chlorine Level (mg/L)	ORP	Relative Estimated Test Lifetime @ 60°C
6.5	5	887	1
6.5	3	873	1.2
8.5	5	778	3.7
8.5	3	758	4.6
6.5	0.1	715	7.7
6.5	0	430	229

Figure 1: Log (Failure Time) versus ORP. Showing data and regression lines for 115°C (pH=6.5) and 105°C (pH=6.5 & 8.5). Non-Failures at 105°C are also shown