

# **THE MECHANISMS OF CHLORINE DIOXIDE OXIDATION OF PLASTIC PIPING SYSTEMS**

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## **ABSTRACT**

There have been several studies on the impact of chlorine on plastic piping systems in potable water applications and methodologies of ensuring performance in the chlorinated water environment have been successfully developed. The impact of chlorine dioxide is less well known. In this paper, laboratory exposed plastic pipe samples are examined to study the impact of chlorine dioxide on oxidative degradation in potable water applications. The mechanisms of oxidation are also characterized.

## **INTRODUCTION**

The use of plastic piping materials in various applications has grown due to the advantages of plastic pipe: durability, resistance to corrosion, installation advantages and cost benefits. In the potable water applications, the plastic piping industry has been proactively developing standards to ensure product performance. Test methodologies (1, 2) have been developed to ensure resistance of plastic piping materials to chlorine which is added to water to maintain the integrity of water through the distribution system.

Test methodologies have mainly been developed around chlorine as it is the most commonly used disinfectant in North America. Globally, the three most commonly used disinfectants are: chlorine, chloramines and chlorine dioxide. These disinfectants are all strong oxidizers. It was previously identified that the macroscopic mechanisms between the three disinfectants are similar (3). In this paper, the oxidation mechanism of chlorine dioxide is further examined.

## **EXPERIMENTAL**

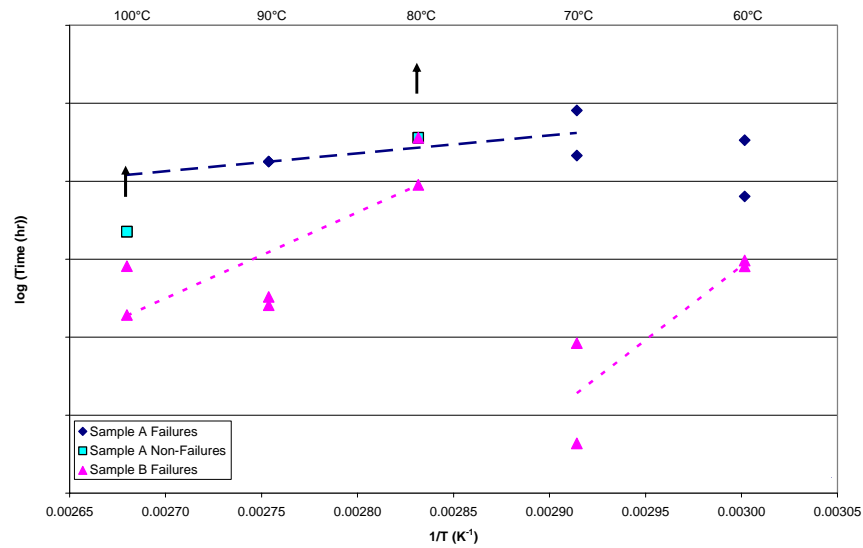
Multiple grades of polyethylene tubing samples were used for testing. Specimens were tested to failure in accordance with the test conditions of ASTM F2263 (2) with the exception of water quality. The water quality was controlled to a chlorine dioxide concentration of 1.0 ppm and a pH of 6.8. Testing was performed at a single stress and multiple elevated temperatures.

## RESULTS

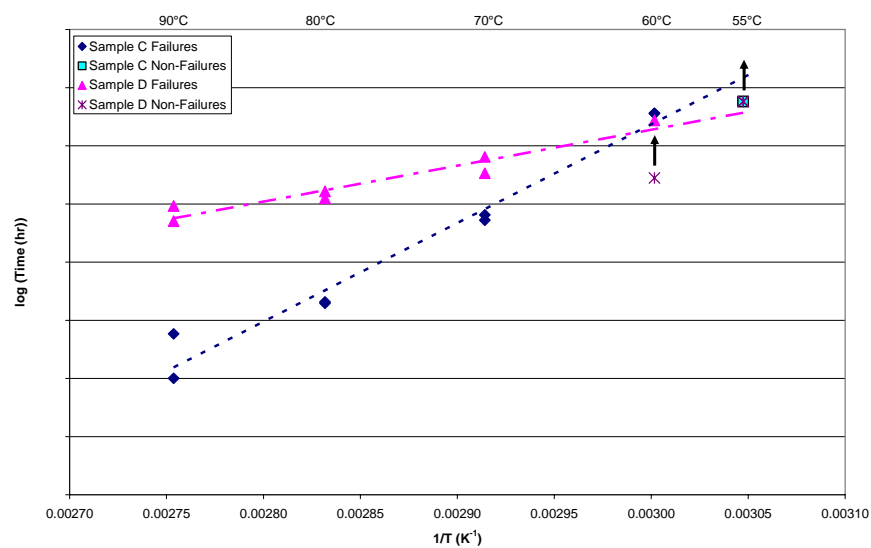
Figures 1 and 2 show the testing to failure results of four PE samples. The results show the following:

- Two of the four samples are observed to have a temperature disconnect between 60 and 80°C (140 to 176°F)
- The remaining two samples appear to have an Arrhenius relationship with temperature over the temperature range of 60 to 90°C (140 to 194°F)

**Figure 1: Failure Times as a Function of Temperature (Samples A and B)**



**Figure 2: Failure Times as a Function of Temperature (Samples C and D)**



## DISCUSSION

The key finding in this research is that there appears to be a temperature discontinuity in chlorine dioxide testing of PE pipe. This phenomenon is not observed in all samples. Several potential reasons have been postulated for the observed inconsistency and the noted temperature disconnect. These theories are listed together below:

1. The chlorine dioxide concentration is changing with temperature
2. There is a change of state of the chlorine dioxide with temperature
3. Variations in the testing are leading to the observed behavior
4. There is a change in the mechanism across the temperature range
5. There is a transition or temperature disconnect between 60 and 80°C (140 to 176°F)

Each theory was examined based on available data and current knowledge. The overall major conclusion from the results is that a non-Arrhenius temperature relationship is observed. As a result, it does not appear to be possible to conduct extrapolations based on the Arrhenius temperature relationship or the Rate Process Model across the entire temperature range. Thus, it is not possible for all materials to be tested at higher temperatures and extrapolate to end-use conditions at the test conditions examined.

## PROPOSED THEORY

Based on the assessment of the results, it is postulated that there may be mechanism shifts due to subtle changes in the failure mechanism and that these mechanism shifts are due to the oxidatively aggressive nature of chlorine dioxide. The theory is discussed in detail below.

### *CRACK INITIATION:*

Crack initiation can be defined as:

$$t_i = BK^n \quad (1)$$

where

$t_i$  = Crack initiation time

$B$  = A material parameter. A pseudo-constant that changes with time due to material degradation

$K$  = Stress intensity factor

$n$  = A constant that may or may not change with material degradation

In an oxidative environment, oxidative aggressiveness also plays a role in crack initiation.

Based on Equation (1), the key factor that differentiates the crack initiation time of different materials is the parameter  $B$ .  $B$  is a pseudo-constant that provides an indication of the inherent resistance of a material to crack initiation and is part of the overall resistance to slow crack growth (resistance to crack propagation being the other key factor). Therefore,  $B$  will be different

for different materials. Materials with higher  $B$  values will have higher resistance to crack initiation and generally higher overall test lifetimes in testing where slow crack growth resistance is a component of the overall failure mechanism.

#### *FACTORS IMPACTING THE RATE OF CHANGE OF $B$ :*

In a non-oxidative environment or prior to degradation in an oxidative environment,  $B$  will remain constant. Therefore, differences in  $B$  values will be reflected in the observed differences in overall lifetimes between materials (i.e. differences in Full-Notch Creep Test (FNCT – ISO 16770 (4)) or Notched Pipe failure times). In an oxidative environment, once degradation has occurred, this may not be the case. To evaluate the impact of degradation on  $B$ , the different factors that influence the rate of overall degradation are examined. They are:

1. Stabilizers and their activity
  - Different stabilizers have different levels of resistance to degradation and as a result, would impact the rate of degradation (and hence the rate of change in  $B$ ) differently
2. Rate of material degradation
  - Once the stabilizer is consumed, the overall rate of degradation is dependent on the rate of material degradation

The rate of material degradation for PE materials will be impacted by the density of the material and its specific polymeric structure. However, because all PE materials have the same C-H backbone, the rate of material degradation is expected to be similar between different PE materials. Therefore, it is postulated that the stabilizer system will play a more dominant role in determining the overall rate of degradation.

Based on the above, it can be postulated that in a very oxidatively aggressive environment, where the stabilizer is quickly consumed and the material quickly degraded, the degradation of the inner surface is such that the “effective”  $B$  value (the  $B$  value after degradation) is similar in the timeframe of the crack initiation process. In other words, the oxidatively aggressive environment “normalizes” the  $B$  values between materials and significant differences in the crack initiation may not be observed under these conditions.

**Figure 3: Postulated Model of  $B$  as a Function of Degradation Level in an Oxidatively Aggressive Environment**

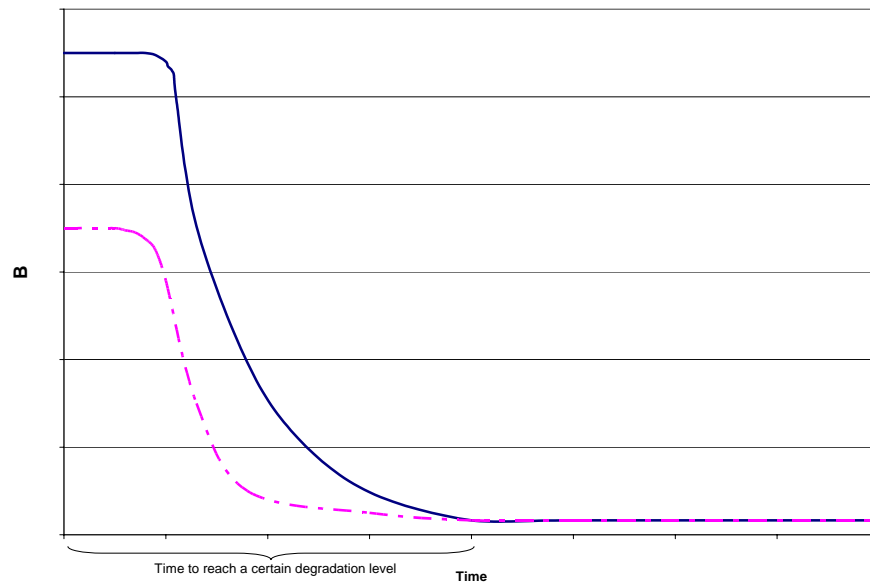


Figure 3 depicts a graphical representation of how exposure to an oxidatively aggressive environment may impact the  $B$  values over time:

- Initial plateau:
  - This region is largely related to the ability of the stabilizer to resist degradation under the tested conditions
  - A more aggressive environment will shorten the length of this plateau and the time to onset of degradation
- The decline:
  - Once the stabilizer is consumed, material degradation begins and the  $B$  value begins to decrease. The steepness of the decline is a function of a material's resistance to degradation
  - A more aggressive environment will increase the steepness of the decline and shorten the degradation time
- Final plateau:
  - This region is related to the inner surface degradation. While the level may be different based on the specific polymer structure, once polymer chains have been broken down into short chains, the  $B$  values are expected to be normalized
  - A more aggressive environment will shorten the time to reach this plateau

It is important to note that, as crack initiation occurs on the inner pipe surface, it is the effective  $B$  value at the inner pipe surface that controls the crack initiation process.

Based on OIT data as a function of time, it is observed that with chlorine dioxide exposure, the stabilizers are consumed relatively quickly compared to what is observed in chlorine exposure. Therefore, the initial plateau would be much shorter with chlorine dioxide exposure.

The shape of the “S” curve would be expected to be different for different materials and different oxidative environments. As well, stress will also play a role in determining what effective  $B$  value the material will have for crack initiation (at higher stresses, crack initiation will occur more quickly, and hence, depending on the relative rates of decrease in  $B$  and crack initiation, crack initiation can occur at higher effective  $B$  values at higher stresses). Therefore, it is possible that at a given stress, one material will have a  $B$  value in the initial plateau region while another material will have a  $B$  value in the decline region. In the overall degradation process, the transition region from one plateau to the other could explain why some materials appear to have disconnects and others do not.

The  $B$  value is mostly dependent on the material’s resistance to degradation and the stabilizer’s resistance to degradation.  $B$  will change with time regardless of stress. However, the stress state will define the actual  $B$  value that the material will experience at a given stress. Depending on the shape of the curve, a material may have high  $B$  values at a high stress state and low  $B$  values at a low stress state. Between materials with different curves, gross differences may be observed in the mode of failure as one material may be pushed from a Mode 4 failure to a Mode 3 failure due to the stress state. This explains how crack initiation is dependent on the stress intensity factor and how the stress intensity factor is tied in with the “effective”  $B$ .

It is also conceivable that, due to the aggressiveness of the chlorine dioxide, the  $B$  values may be in the second plateau region at crack initiation. Different materials with large differences in initial  $B$  values may, therefore, exhibit similar effective  $B$  values at crack initiation.

The overall result would be that chlorine dioxide shifts the timescale due to its aggressiveness and as a result, acts as an “equalizer” between materials in their resistance to crack initiation. In other words, in chlorine dioxide, the effective  $B$  cannot be differentiated between materials.

#### *CRACK PROPAGATION:*

Crack propagation has similar events that occur compared to crack initiation.

It is dependent on the stress intensity factor and also contains a material parameter that is a pseudo-constant. It is postulated that there is an interplay of variables based on the stress state, the material and temperature similar to that discussed for crack initiation.

Differences in the effective stress can also be observed during testing at different temperatures. Therefore, it is possible to test at the same stress at two temperatures and see a different balance

between the Mode 3 and Mode 4 failure regimes. This could also contribute to the observed temperature disconnect.

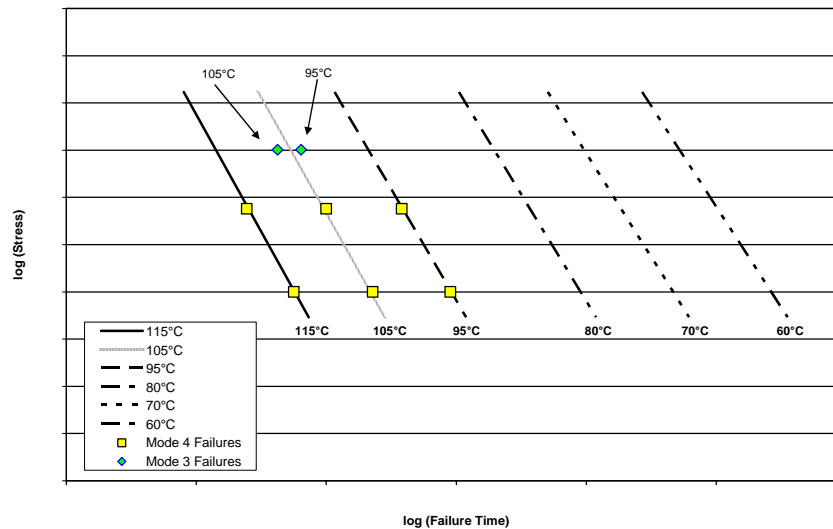
### *SHIFTS IN MECHANISM:*

It has been established that shifts in failure mechanisms occur for polyolefin materials from ductile to brittle to brittle oxidative failure (Stages I, II and III) as stress decreases. Other potential shifts in mechanisms are discussed in this section.

#### *Mode 3/Mode 4 Shift Mechanism*

One known shift in mechanism is between Mode 3 (oxidative initiation-mechanical propagation) and Mode 4 (oxidative initiation-oxidative propagation) type failures (5). As shown in Figure 4, an apparent and unusual temperature and stress behavior is observed when the failure mode changes from Mode 4 to Mode 3. The temperature dependence is observed to change drastically with a change in the failure mode. This Mode 3/Mode 4 shift mechanism has been observed for PEX materials tested in chlorine, generally at higher test stresses. It would appear that the Mode 3/Mode 4 shift mechanism acts as an “equalizer” on the temperature variable such that the impact of temperature is not as significant in this shift zone as it is in the Mode 4 region. This is demonstrated in the data presented in Figure 4 for a PEX material tested in chlorinated water.

**Figure 4: Example of a PEX Material Tested in Chlorinated Water Showing a Disconnect Between Mode 3 and Mode 4 Failures**



#### *Mechanical/Chemical Shift Mechanism*

Crack initiation is dependent on both material degradation (the pseudo-constant material parameter) and the physical crack initiation (the stress intensity factor). Each component has a

different temperature dependence. Therefore, the balance between the chemical (material degradation) and the mechanical (physical crack initiation) factors can shift with temperature. The rate of change of material pseudo-constants appears to be higher for chlorine dioxide than chlorine (and oxygen) due to the highly aggressive nature of chlorine dioxide. As a result, more significant changes in the balance between mechanical and chemical processes for crack initiation (and/or propagation) may occur with chlorine dioxide exposure.

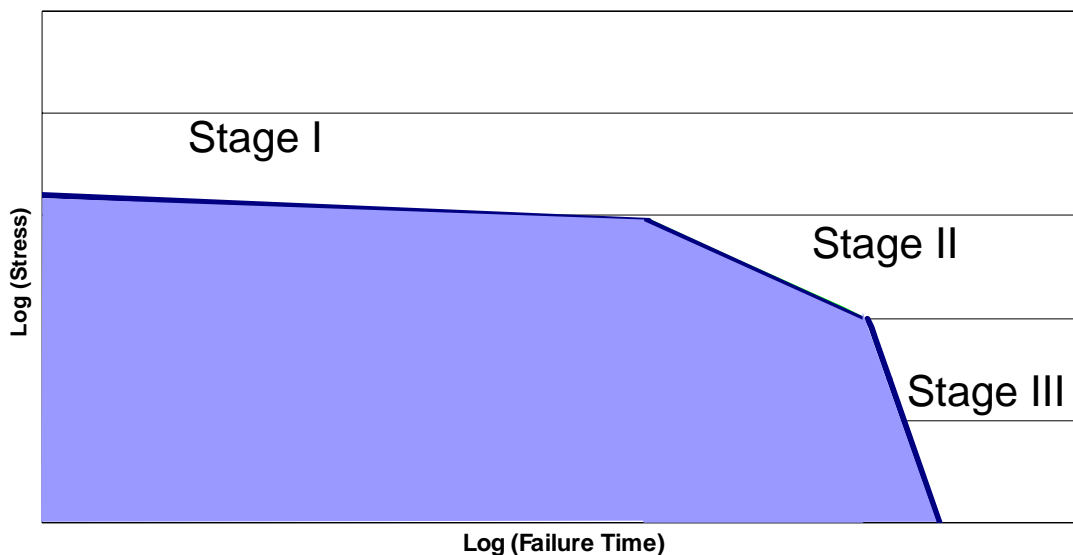
The specific variables involved are:

- Material resistance to slow crack growth (effective  $B$ )
- Time
- The oxidative environment/oxidant
- Stress
- Temperature

### *Stress Shift Mechanism*

As discussed above, there is a balance in the impact of the mechanical and chemical processes on overall failure. As shown in Figure 5, at high stresses, the mechanical process overpowers the chemical process. At lower stresses, the chemical process has a greater impact and the impact of stress is not as significant. As shown by the slope of the Stage III oxidative failure line, the relative impact of stress on lifetime is much lower than in Stages I and II. Therefore, it appears that the oxidative environment acts as an “equalizer” on stress.

**Figure 5: Typical Failure Curve with Stage I, II and III Failures**



### *Mechanism Shift Boundaries (MSBs)*

Mechanism Shift Boundaries (MSBs) are defined as the regions/boundaries of test variables where a shift in the mechanism occurs. As discussed above, three MSBs have been identified:

1. Mode 3/Mode 4 MSB
2. Mechanical/Chemical MSB
3. Stress MSB

Each MSB is dependent on specific parameters:

- The aggressiveness of the environment
- The temperature
- The stress
- The material

MSBs are expected to be different for different materials as materials could show different behavior and different transition points. As well, the “equalization” effects would also be expected to be different for different materials.

### *The Intersection of MSBs*

It is conceivable that, at a given temperature and stress condition, a situation could occur where there is an intersection of MSBs. If such a situation occurred, it would result in a highly complex interplay of factors and apparently “inexplicable” and, hence, unpredictable stress and temperature behavior. This appears to have occurred in the chlorine dioxide testing because of the aggressiveness of chlorine dioxide compared to chlorine. The aggressiveness appears to have shifted some of the mechanisms such that they now fall within MSBs. This could explain the atypical results and why the trends are not consistent between samples. It should also be noted that a few instances of similar unusual stress and temperature behavior have also been observed in chlorine testing of PE materials.

## **CONCLUSIONS**

Overall, it would appear that there are competing factors and, as well, shifts in mechanisms that are occurring in chlorine dioxide testing of PE materials. These shifts have been observed in chlorine testing and for PEX materials. However, it would appear that in chlorine testing and PEX testing, there are fewer competing factors and a lower likelihood of interactions between MSBs. As a result, this allows for selection of conditions such that a relevant Arrhenius relationship can be developed. With chlorine dioxide testing, due to the aggressiveness of chlorine dioxide, the situation appears to be more complex such that an Arrhenius relationship (and, therefore, the Rate Process Model) is not suitable across the test conditions examined (for all materials). Alternative methods of testing are being examined.

## ACKNOWLEDGEMENTS

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